PB85-188837

Assessment of PCDDs (Polychlorinated Dibenzodioxins) and PCDFs (Polychlorinated Dibenzofurans) from PCB (Polychlorinated Biphenyl's) Transformer and Capacitor Fires

Technical Resources, Inc., Bethesda, MD

Prepared for

Environmental Protection Agency, Cincinnati, OH

Apr 85

U.S. Department of Commerce
National Technical Information Service
NTIS

PB85-188837

EPA/600/2-85/036
April 1985

ASSESSMENT OF PCDDs AND PCDFs FROM PCB TRANSFORMER AND CAPACITOR FIRES

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TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA/600/2-85/036	**2.**	**3. RECIPIENT'S ACCESSION NO.** PB85 188837/AS
4. TITLE AND SUBTITLE Assessment of PCDDs and PCDFs from PCB Transformer and Capacitor Fires		**5. REPORT DATE** April 1985
		6. PERFORMING ORGANIZATION CODE -
7. AUTHOR(S) Anthony Lee		**8. PERFORMING ORGANIZATION REPORT NO.**
9. PERFORMING ORGANIZATION NAME AND ADDRESS Technical Resources, Inc. 3202 Monroe Street, Suite 300 Rockville, Maryland 20852		**10. PROGRAM ELEMENT NO.**
		11. CONTRACT/GRANT NO. 68-03-3212
12. SPONSORING AGENCY NAME AND ADDRESS HAZARDOUS WASTE ENGINEERING RESEARCH LABORATORY OFFICE OF RESEARCH AND DEVELOPMENT U.S. ENVIRONMENTAL PROTECTION AGENCY CINCINNATI, OH 45268		**13. TYPE OF REPORT AND PERIOD COVERED**
		14. SPONSORING AGENCY CODE EPA/600-12

15. SUPPLEMENTARY NOTES

16. ABSTRACT

The EPA, under the Toxic Substances Control Act, has been mandated to develop appropriate regulations for the control of exposure to polychlorinated biphenyls (PCBs). In light of this responsibility the EPA Office of Toxic Substances recently issued an Advance Notice of Proposed Rulemaking (ANPR) intended to define the problem of releases of PCBs and other toxic compounds during fires involving transformers and capacitors containing PCBs.

The EPA Office of Research and Development (ORD) has also been mandated under the recently released Dioxin Strategy document to evaluate fire accidents involving PCB transformers and capacitors as potential new sources of polychlorinated dibenzodioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) in the environment. To develop the information to support the two mandated programs, the EPA/ORD undertook this study to assess the problems associated with fires involving askarels, to catalog the contamination experiences and to review potential decontamination methods as well as disposal of contaminated material.

This study assesses the chemistry of PCBs under thermal conditions and evaluates the generation of PCDDs and PCDFs. It reviews technologies for destruction and disposal of PCBs and their toxic contaminants. Methodologies to assess potential hazards and reduce exposure are also discussed.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

18. DISTRIBUTION STATEMENT Release Unlimited	**19. SECURITY CLASS** *(This Report)* Unclassified	**21. NO. OF PAGES** 129
	20. SECURITY CLASS *(This page)* Unclassified	**22. PRICE**

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE

NOTICE

This document has been reviewed in accordance with U.S. Environmental Protection Agency policy and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

Today's rapidly developing and changing technologies and industrial products and practices frequently carry with them the increased generation of solid and hazardous wastes. These materials, if improperly dealt with, can threaten both public health and the environment. Abandoned waste sites and accidental releases of toxic and hazardous substances to the environment also have important environmental and public health implications. The Hazardous Waste Engineering Research Laboratory assists in providing an authoritative and defensible engineering basis for assessing and solving these problems. Its products support the policies, programs and regulations of the Environmental Protection Agency, the permitting and other responsibilities of State and local governments and the needs of both large and small business in handling their wastes responsibly and economically.

This report describes the occurrence of toxic chlorinated organic compounds resulting from combustion or pyrolysis of transformer and capacitor dielectric fluids containing polychlorinated biphenyls (PCBs). Results from accidental fires in buildings as well as from the scientific literature are presented. The report will be useful to the electric utility industry, the fire fighting profession and the hazardous waste research and regulatory communities. For further information, please contact the Alternative Technologies Division of the Hazardous Waste Engineering Research Laboratory.

David G. Stephan, Director
Hazardous Waste Engineering Research Laboratory

ABSTRACT

The discovery of toxic contaminants such as polychlorinated dibenzofurans (PCDFs) in PCBs and askarel fluids has elevated the environmental and health concerns associated with PCB transformers and capacitors. The EPA Office of Research and Development (ORD) is mandated under EPA's recently-released Dioxin Strategy document to evaluate fire accidents involving PCB transformers and capacitors as potential new sources of PCDDs and PCDFs in the environment. To develop the necessary information, the EPA/ORD undertook this study to assess the problems associated with fires involving askarels, to catalog the contamination experiences and to review emergency response measures and decontamination protocols. This study assesses the chemistry of PCBs under thermal conditions and evaluates the generation of PCDDs and PCDFs. It draws upon the present knowledge on the thermodynamic equilibria of chlorinated substances and the more common experiences gained from decontamination and detoxification of PCBs in non-fire accident situations. It documents the emergency response and decontamination protocols and summarizes technologies for destruction and disposal of PCBs and their toxic contaminants.

This report was submitted in fulfillment of Contract No. 68-03-3212 by Technical Resources, Inc., Rockville, Maryland, under the sponsorship of the U.S. Environmental Protection Agency. This report covers a period from February 1984 to July 1984, and was completed as of August 31, 1984.

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ABBREVIATIONS

AC	alternating current
ACGIH	American Conference of Governmental Industrial Hygienists
AFFF	aqueous film forming foam
ANPR	advance notice of proposed rulemaking
APCS	air pollution control system
C	centigrade
CDD	chlorodibenzodioxin
CDF	chlorodibenzofuran
cm	centimeter(s)
cm^2	square centimeter(s)
d	day(s)
DCDD	dichlorodibenzodioxin
DEC	New York State Department of Environmental Conservation
dm^2	square decimeter(s)
DOH	New York State Department of Health
EPA	United States Environmental Protection Agency
F	Fahrenheit
FPLC	Florida Power and Light Company
ft	foot or feet
g	gram(s)
gal	gallon(s)
GC/HRMS	gas chromatograph/high resolution mass spectrometer
GC/MS	gas chromatograph/mass spectrometer
HCDD	hexachlorodibenzodioxin
hr	hour(s)
HRGC/MS	high resolution gas chromatograph/mass spectrometer
HVAC	heating, ventilation and air conditioning
Hz	hertz or cycle(s) per second
IAFF	International Association of Fire Fighters
I.D.	inside diameter
IERL-Ci	Industrial Environmental Research Laboratory-Cincinnati
kg	kilogram(s)
kv	kilovolt(s)
kVA	kilovolt - ampere(s)
L	liter
lbs	pounds
LC	liquid chromatograph

m	meter(s)
m^2	square meter(s)
m^3	cubic meter(s)
M	molar
mcg	microgram(s)
mcl	microliter(s)
mcm	micrometer(s)
ml	milliliter(s)
m.p.	melting point
n.d.	not detected or none detected
ND	not detected or none detected
NEC	National Electrical Code
ng	nanogram(s)
NIOSH	National Institute for Occupational Safety and Health
OCDD	octachlorodibenzodioxin
OGS	New York State Office of General Services
ORD	Office of Research and Development
OSHA	Occupational Safety and Health Administration
PCB	polychlorinated biphenyl
PCBP	polychlorinated biphenylene
PCCY	polychlorinated chrysene
PCDD	polychlorinated dibenzodioxin
PCDE	polychlorinated diphenylether
PCDF	polychlorinated dibenzofuran
PCN	polychlorinated naphthalene
PCP	pentachlorophenol
PCPY	polychlorinated pyrene
pg	picogram(s)
PG&E	Pacific Gas and Electric Company
PIC	product of incomplete combustion
ppb	parts per billion
ppm	parts per million
ppt	parts per trillion
PVC	polyvinyl chloride
RFP	request for proposal
SCBA	self-contained breathing apparatus
sec	second(s)
TCDD	tetrachlorodibenzodioxin
TCDF	tetrachlorodibenzofuran
TSCA	Toxic Substances Control Act
TWA	time-weighted average
ug	microgram(s)
wt	weight

SECTION 1

INTRODUCTION

Polychlorinated biphenyls (PCBs) are a class of compounds that have various combinations of chlorine atoms attached to the biphenyl molecule. Since commercial introduction in the late 1920s, over 1.25 billion pounds of PCBs have been manufactured and used in the U.S., primarily in mixtures with chlorobenzenes known as askarels which are used as dielectric fluids for electrical transformers and capacitors, heat transfer systems, and hydraulic systems. A large amount of PCBs sold in the USA is still in use as dielectric fluid in capacitors and transformers (1).

Federal regulation of PCBs took several years to develop. Beginning in the late 1960's, scientific evidence began to accumulate on PCBs' various toxic effects and concentration in many biological species. Because of these concerns, in 1971, the Monsanto Industrial Chemical Co., the sole United States producer, terminated sales of PCBs for all but closed electrical systems uses (1). In 1976, Congress enacted the Toxic Substances Control Act (TSCA) and included special provisions for the regulation of PCBs. Accordingly, in 1979, EPA banned all production and sales of PCBs. Follow-on regulations enacted under the Toxic Substances Control Act now govern the disposal of PCBs and PCBs-containing equipment (2).

Recently, there have been additional concerns brought on by the finding of other toxic contaminants in PCBs and askarel fluids including polychlorinated dibenzofurans (PCDFs), chlorinated benzenes and other chlorinated substances. PCDFs and the other chlorinated substances are formed as contaminants in the manufacturing and formulation processes for PCBs and askarel fluids. Polychlorinated dibenzodioxins (PCDDs) can be formed from the reaction of chlorinated benzenes when askarel fluids are heated to a very high temperature (3). The finding of PCDFs and the potential generation of PCDDs under thermal conditions has major implications for the recently-adopted EPA strategy in mitigating and controlling chlorinated dioxins in the nation's environment. Findings of such toxic chemicals will also further complicate emergency response and clean-up procedures for fires involving PCBs-containing transformers and capacitors.

Several such fires have been reported. The most famous is the fire involving a transformer that occurred in an 18-story office building in Binghamton, New York on February 5, 1981. The transformer contained 65% Aroclor 1254 (a Monsanto PCBs product trade name) and 35% chlorinated benzenes together with some other additives. Analyses of soot samples taken from the building showed high levels of PCBs, and the presence of 2,3,7,8-tetrachlorodibenzo(p)dioxin (2,3,7,8-TCDD) and 2,3,7,8-tetrachlorodibenzofuran (2,3,7,8-TCDF) (4). The estimated clean-up cost for the building is $24 million and almost $1 billion in liability claims have been filed against the state in law suits filed primarily by the fire fighters (5).

Similar cases have been reported in other parts of the country as well as in foreign countries such as Sweden and Finland. These accidents have led to the need for assessing potential environmental loading of PCDDs and PCDFs and human exposure risk from this new source category. Additionally, because such fire accidents have occurred randomly in office buildings, schools, etc., and not only in industrial plants, there is a high public awareness of this issue. Thus, there is a genuine public concern over potential exposure to highly toxic substances (i.e., dioxins and furans) from such fire incidents.

Fire fighters, electric utility companies and insurance companies are particularly concerned that fire emergency procedures and fire site clean-up protocols may not be adequate in light of these new findings. Present fire fighting methods were developed when the hazards of exposure to highly toxic chemicals were not as well understood. In an already dangerous profession, fire fighting personnel must now recognize the danger of exposure to hazardous chemicals with potential long term health implications.

The EPA, under the Toxic Substances Control Act, has been mandated to develop appropriate regulations for the control of exposure to PCBs. In light of this responsibility the EPA Office of Toxic Substances recently issued an Advance Notice of Proposed Rulemaking (ANPR) intended to further define the problem (6). The ANPR is intended to cover the following areas:

- Risks associated with PCB transformer and capacitor fires
- Number and distribution of PCB transformers and capacitors
- Location of equipment
- Frequency of fires
- Furan/dioxin formation
- Regulatory options.

The EPA Office of Research and Development (ORD) has also been mandated under EPA's recently-released Dioxin Strategy document to evaluate fire accidents involving PCB transformers and capacitors as potential new sources of PCDDs and PCDFs in the environment (7). To develop the information to support the two mandated programs, the EPA/ORD undertook this study to assess the problems associated with fires involving askarels, to catalog the contamination experiences and to review potential decontamination methods as well as disposal of contaminated material. The study recognized the limitation of available data. It has drawn upon the body of scientific knowledge available on thermodynamic equilibria of chlorinated substances and the more common experiences gained from decontamination and detoxification of PCBs in non-fire accident situations. This study assesses the chemistry of PCBs under thermal conditions and evaluates the generation of PCDDs and PCDFs. It reviews technologies for destruction and disposal of PCBs and its toxic contaminants. Methodologies to assess potential hazards and reduce exposure are also discussed.

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SECTION 2

CONCLUSIONS AND RECOMMENDATIONS

Approximately 130,000 transformers and 2.8 million capacitors currently in service contain PCBs or a mixture of PCBs and trichlorobenzenes which is also called askarels. There have been a number of fire accidents involving PCBs transformers and capacitors throughout the world. The two most infamous involve the two office building complexes in Binghamton, New York and San Francisco, California where widespread contamination occurred.

Analysis of soot samples from PCBs transformer and capacitor fire incidents indicate that a number of highly toxic chlorinated products are formed including polychlorinated dibenzofurans (PCDFs) and polychlorinated dibenzodioxins (PCDDs). Laboratory combustion studies on PCBs have identified a variety of other chlorinated products such as polychlorinated naphthalenes, pyrenes, biphenylenes and chrysenes.

The types of chlorinated products that are formed depend on the composition of the fluid in the transformer or capacitor. In the Binghamton incident, both PCDDs and PCDFs were identified whereas in San Francisco, only PCDFs were found. The Binghamton transformer contained a mixture of PCBs (Aroclor 1254) and trichlorobenzenes and the San Francisco transformer contained only PCBs. The finding of PCDDs in the Binghamton incident is attributed to chemical reactions involving trichlorobenzenes present in the transformer fluid.

The presence of highly toxic substances such as PCDFs and PCDDs in PCBs fire incidents has elevated concerns for the safety of emergency response personnel and complicated clean-up and remedial measures. There is an obvious need for the development of a generally accepted protocol for fighting and extinguishing fires involving PCBs electrical equipment.

Electrical utilities can assist local fire fighting departments with better information on the problems associated with PCBs fires. Fire departments should know the number and location of PCBs transformers and capacitors within their jurisdictions. Highly visible labels or signs should be placed on all PCBs-containing electrical equipment and in other nearby areas to indicate the presence of PCBs-containing electrical equipment. Electrical utilities, owners and/or operators of the equipment should retrofit the equipment to assure that electrical power could be rapidly disconnected in the event the transformer enters a failure mode. The primary load breaker air switch on the high-voltage side of the transformer should be located outside of the equipment vault to allow rapid disconnect without entering the vault containing high concentrations of PCBs and associated pyrolysis products.

Response operations during the initial phase of a fire incident involving PCBs-containing transformers and capacitors requires familiarity with response organization and management, the uses and limits of equipment and apparatus, site entry, control, and decontamination procedures. In order to control and handle PCB fire situations, adequate protective clothing, equipment and fire extinguishing chemicals are necessary to ensure personnel safety.

PCBs transformer/capacitor fires are unique because of the toxic residues generated and the resultant long-lasting contamination. Every effort should be made to put out the fire as quickly as possible in order to minimize the production of highly toxic pyrolysis products. After the fire, access to areas possibly contaminated by the fire must be limited until the extent of contamination can be determined. Wipe and bulk soot sampling are used to identify PCBs contaminated areas, and to delineate the extent of both vertical and horizontal contamination.

There are no Federal guidelines to define acceptable clean-up for PCBs releases due to fires. NIOSH has found background levels in urban areas up to 0.5 mcg PCBs/100 cm^2 of surface area. In the absence of certain PCDF and PCDD isomers, the mitigation effort could be directed at clean-up of the PCBs contamination to 0.5 mcg per 100 cm^2 of affected area. In terms of airborne exposure the NIOSH recommended guideline for the workplace is 1.0 mcg PCBs per m^3 of air.

The presence of PCDF and PCDD isomers will affect surface and air clean-up guidelines according to the biological and toxicological activity of the specific isomers. Reoccupancy criteria have been established by the State of New York and the State of California following the Binghamton and the San Francisco fires. The State of New York proposed an average daily intake of 2 pg/kg/d for 2,3,7,8-TCDD, resulting in an air/inhalation exposure limit of 10 pg/m^3 for 2,3,7,8-TCDD. A limit of 39 pg/m^3 for 2,3,7,8-TCDF was proposed. The State of California proposed air exposure guidelines of 10 pg/m^3 for 2,3,7,8-PCDDs/PCDFs, 1.0 mcg/m^3 for PCBs. The criteria for surface exposure are 3 ng/m^2 for 2,3,7,8-PCDDs/PCDFs and 100 mcg/m^2 for PCBs. In addition to these values for decontaminated areas outside of the transformer vault, the State of California proposed reentry guidelines for the area inside the vault. These consist of an air exposure of 80 pg/m^3 for 2,3,7,8-PCDDs/PCDFs and 1.0 mcg/m^3 for PCBs and a surface exposure of 24 ng/m^2 for 2,3,7,8-PCDDs/PCDFs and 1.0 mg/m^2 for PCBs. Sweden and Finland have also established reoccupancy criteria after the occurrence of PCBs fire incidents.

SECTION 3

PCB TRANSFORMERS AND CAPACITORS

TYPES OF TRANSFORMERS

Transformers are used to raise or lower electric voltage and generally consist of a core and a coil immersed in a dielectric fluid. A list of the 13 companies which manufactured askarel transformers in 1975 is given in Table 1 (1, 2). At electric generating utility facilities, large transformers are used to raise voltage. As the electrical power is sent through the transmission and distribution system(s) the voltage may be raised or lowered a number of times to meet the technical configuration of the system and the voltage requirements of the customer.

A large transformer may be several times larger than an automobile and contain hundreds to thousands of gallons of oil and dielectric fluid. Such transformers are typically located in generating facilities or substations. Most transformers are considerably smaller and are often mounted on utility poles located throughout the distribution systems. These overhead transformers are used to lower voltage to a level usable by private residences or small businesses, and typically contain an average of 20 gallons of fluid.

Between the large transformers used to transmit power and the small overhead transformers used to bring power into homes, there are a number of transformers of assorted sizes and voltage ratings designed to meet the requirements of various commercial, industrial, and resale customers. Where these transformers are located indoors, local fire codes often specify the use of PCBs as the insulating fluid, since PCBs are less combustible than mineral oil.

According to the National Electrical Manufacturers Association, all transformers can be classified into five categories:

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Table 1. U.S. TRANSFORMER MANUFACTURING INDUSTRY USING PCBs IN 1975 (1, 2).

Company Name	Location of Plant	PCBs Trade Name
Westinghouse Electric Corp.	South Boston, VA Sharon, PA	Inerteen
General Electric Company	Rome, GA Pittsfield, MA	Pyranol
Research-Cottrell	Finderne, NJ	
Niagara Transformer Corp.	Buffalo, NY	EEC-18
Standard Transformer Co.	Warren, OH Medford, OR	
Helena Corp.	Helena, AL	
Hevi-Duty Electric	Goldsboro, NC	
Kuhlman Electric Co.	Crystal Springs, MS	Saf-T-Kuhl
Electro Engineering Works	San Leandro, CA	
Envirotech Buell	Lebanon, PA	
R.E. Uptegraff Mfg. Co.	Scottsdale, PA	
H.K. Porter	Belmont, CA Lynchburg, VA	
Van Tran Electric Co.	Vandalia, IL Waco, TX	

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- Large Power Transformers
- Small Power Transformers
- Distribution Transformers
- Network Transformers
- Instrument and Special Purpose Transformers.

Large Power Transformers

Large Power Transformers are liquid-immersed with a capacity range greater than 10,001 kVA. There are two subcategories:

- Conventional Transformers and Autotransformers
- Primary and Secondary Unit Substation Transformers.

Small Power Transformers

Small Power Transformers are basically the same as the Large Power Transformers except their ratings range from 501 to 10,000 kVA. There are three subcategories:

- Conventional Transformers and Autotransformers
- Secondary Unit Substation Transformers and Single Circuit Substations
- Primary Unit Substation Transformers.

Distribution Transformers

Distribution Transformers are liquid immersed ranging from 500 kVA and smaller. Based on their installation, there are three types:

a) Overhead

They are usually located on the top of office buildings, schools, hotels and highly populated structures where fire safety is an important consideration.

b) Pad-mounted

They are installed on a concrete pad outside the area they serve and are usually found in less populated locations.

c) Sub-surface

They are installed underground such as in subways and the basements of buildings.

Network Transformers

Network Tranformers are a special arrangement of transformers to distribute the electrical load to form a network system. There are two types:

a) Grid type secondary network system

These systems are most commonly employed in a high density load location such as in the metropolitan areas. This grid system prevents service interruption to any load on the system because if the power supply to any load is lost, that load will be serviced by the other power sources in the system.

b) Spot network system

Spot network uses two or more transformers. Such networks provide service reliability and operating flexibility in downtown, high-density areas and are being applied frequently in outlying areas for large commercial services where the supply feeders can be made available.

Instrument and Special Purpose Transformers

There are special purpose transformers to serve specific functions and they include:

- Reactors
- Furnace Transformers

- Rectifier Transformers
- Locomotive Transformers
- Grounding Transformers
- Ground Fault Neutralizers
- Mobile Transformers
- Mobile Unit Substations
- Integral Single Circuit Unit Substation.

TYPES OF CAPACITORS

Through the use of transformers, power system engineers raise or lower voltages to meet consumers' requirements. However, much more precise control of electric power is required. Capacitors are commonly used to improve distribution voltage levels by improving the system power factor. This has the net effect of reducing load on certain power system components, such as transformers, cables, and generators.

Capacitors are located throughout a utility system network, both in substations and mounted on poles in the distribution system. Fifty-six percent of utility capacitors are located in substations or generating facilities and the remainder are located in distribution systems. Their precise number and location in a system is purely a function of how the system is designed to meet the requirements of its customers.

The physical size of capacitors does not vary as much as that of transformers. Most are approximately two feet by one foot by six inches and contain approximately 2-3 gallons of fluid.

Virtually all capacitors manufactured prior to 1978 were filled with PCBs. The concentration of PCBs in a PCB capacitor is known to approximate 100%. Those manufactured since 1978 contain a variety of fluids, excluding mineral oil. Table 2 is a list of 17 companies manufacturing PCB capacitors in 1975 (1, 2).

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Table 2. U.S. CAPACITOR MANUFACTURING INDUSTRY USING PCBs IN 1975 (1, 2).

Company Name (In Order of PCBs Usage)	Location of the Plant	PCBs Trade Name
General Electric Company	Hudson Falls, NY Ft. Edward, NY	Pyranol
Westinghouse Electric Corp.	Bloomington, IN	Inerteen
Aerovox	New Bedford, MA	Hyvol
Universal Manufacturing Corp.	Bridgeport, CT Totowa, NJ	
Cornell Dubilier	New Bedford, MA	Dykanol
P.R. Mallory & Co., Inc.	Waynesboro, TN	Aroclor B
Sangamo Electric Co.	Pickens, SC	Diaclor
Sprague Electric Co.	North Adams, MA	Chlorinol
Electric Utility Co.	LaSalle, IL	Eucarel
Capacitor Specialists, Inc.	Escondido, CA	
JARD Corp.	Bennington, VT	Clorphen
York Electronics	Brooklyn, NY	
McGraw-Edison	Greenwood, SC	Elemex
RF Interonics	Bayshore, NY	
Axel Electronic, Inc.	Jamaica, NY	
Tobe Deutschmann Labs.	Canton, MA	
Cine-Chrome Lab, Inc.	Palo Alto, CA	

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The number of PCB capacitors currently in service is estimated to be approximately 2.8 million units (3), and approximately 400,000 non-PCB units (i.e., large capacitors generally containing less than 50 ppm of PCBs) have been acquired since 1978.

Two important types of capacitors are phase correctors on power lines and ballast capacitors for fluorescent lighting. The principal types of PCBs impregnated capacitors are (1):

- High Voltage Power Capacitors
- Low Voltage Power Capacitors
- Lighting Capacitors
- Air Conditioning Capacitors
- Industrial Electronics Capacitors.

High Voltage Power

Generally AC capacitors are used to improve the power factor of a circuit. The power factor is the ratio of true power in watts to the apparent power as obtained by multiplying the current flowing to the load by the circuit voltage. The power factor correction can be made directly at the load or at utility substations. In the latter case, high voltage units will be designed for 4,800 to 13,800 volt service.

Low Voltage Power

Capacitors installed in industrial plants at the demand site (typically large motors and welders) are designed for 230- to 575-volt service. Capacitors installed near the loads are the most efficient way to supply the electrical current which is converted to magnetizing current, to produce the flux necessary for the operation of inductive devices. Rates for the sale of power are generally structured to encourage power factor correction at the site, eliminating the need for the electric utility to transmit both powerproducing current and magnetizing current all the way from the generator to the plant site.

The same considerations apply to induction heating applications, the principal difference being that capacitors for this application are designed for operation at 960 to 9600 Hz. These low voltage power factor capacitors operate most efficiently at a voltage of 400 volts/mil (1).

Lighting

Capacitors improve the efficiency of lighting systems. A fluorescent or mercury vapor lamp can be ballasted without the use of a capacitor, but the power factor of the lighting system would then be in the range of 50 to 60%. For commercial or industrial lighting with either fluorescent or high intensity discharge lamps, the use of a capacitor in the circuit provides part of the lamp ballasting and brings system power factor into the range of 90 to 95%.

Air Conditioning

As in the lighting applications, the capacitor improves system efficiency. Air conditioners could be made to operate without capacitors, as do home refrigerators, but because of the higher capacity required for air conditioners, the resultant line current would virtually eliminate home "plug-ins" and would still further overburden a seriously threatened national power network. Almost all air conditioner pump motors are of the split-winding type on which the capacitor provides phase differential for the so-called start winding, thus delivering good starting torque. The proper size capacitor permits a high (90%) power factor after start-up.

Industrial Electronics

This market category is a catch-all covering many varied applications, two important ones being motor run and power supply applications. Motor run applications are for pumps, fans, and farm feed equipment, and do not differ significantly from air conditioning applications. The power supply market uses capacitors principally to provide a high power factor, but through careful design a capacitor can also provide wave shaping where desired.

TYPES OF TRANSFORMER FLUID

There are two commonly used transformer fluids:

- Mixtures of PCBs and Trichlorobenzene
- Mineral Oil.

PCBs/Trichlorobenzene Transformers

The mixtures of PCBs and trichlorobenzenes are commonly known by the generic term askarels. Askarels are usually mixtures of ~70 percent PCBs and 30 to 40 percent trichlorobenzenes. Further information about the chemical composition of askarels can be found in Sections 4 and 6.

The volume of askarel used in various transformers ranges from 40 to 1500 gallons (440 to 17,000 lbs), with an average of about 230 gallons (2500 lbs). It is estimated that the total number of askarel-filled transformers still in service in the United States is 130,000. The typical lifetime of a transformer is often greater than 30 years, and units that do fail are usually rebuilt and returned to service. The production of askarel-filled units was stopped in 1979 after the ban of PCBs production by the EPA. Table 3 provides the average number of gallons per transformer for each size range.

A graph of the average number of gallons versus transformer size using the data of Table 3 is in Figure 1. This graph can be used to estimate the volume of askarel fluid in the transformer for a given kVA rating.

Table 3. VOLUME OF FLUID CONTAINED IN ASKAREL TRANSFORMERS (3).

Transformer Size (kVA Rating)	Average Number of Gallons per Transformer	Total Number of Gallons of Fluid
≤100	43	570,000
101-500	180	2,113,000
501-1,000	330	3,240,000
1,001-5,000	490	2,336,000
5,001-100,000	1,700	266,000
TOTAL		8,525,000

Mineral Oil Transformers

PCBs are also present in mineral oil transformers at various concentrations but usually at less than 10 ppm. A substantial portion of the PCBs is present at concentrations of 100 to 500 ppm and mainly located in small transformers. Tables 4 and 5 show the distribution of PCBs concentrations for mineral oil transformers.

As can be seen, 10 percent of the transformers are contaminated at levels of 50 ppm or greater. As illustrated in Table 6, contamination levels do not appear to be significantly related to the size of the equipment. The age of the equipment was also analyzed in relation to contamination levels, and no significant correlation was found.

Table 7 indicates the percentage of transformers containing PCBs at a concentration of less than 50 ppm. Table 8 provides data regarding the total volume of mineral oil contained in mineral oil transformers owned by the utility industry, as well as the average number of gallons per transformer reported for each size range.

Thirty-nine percent of this oil is contained in transformers located in substations or generating facilities. A graph of the average number of gallons versus transformer size was plotted in Figure 2. The data are taken from Table 8. This graph can be used to estimate the number of gallons of fluid in the mineral oil transformer for a given kVA rating.

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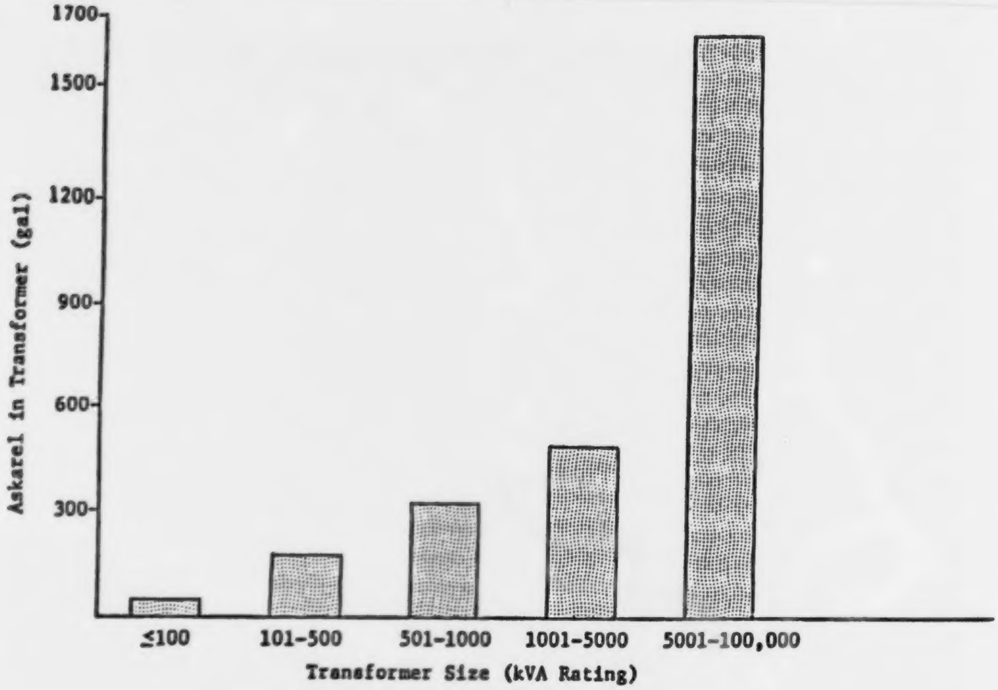

Figure 1. Askarel Transformer - Gallons vs Rating

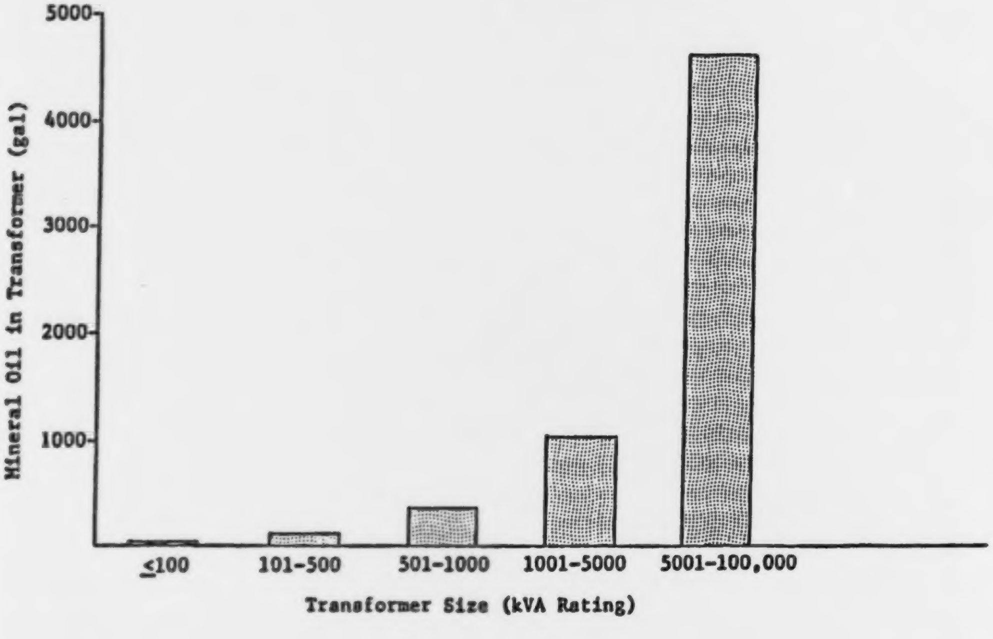

Figure 2. Mineral Oil Transformer - Gallons vs Rating

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Table 4. DISTRIBUTION OF PCBs CONCENTRATIONS FOR MINERAL OIL TRANSFORMERS (3).

PCBs Concentration (ppm)	Percent of Transformers
<1	46.1%
1-9.9	27.8
10-19.9	6.8
20-29.9	4.3
30-39.9	2.1
40-49.9	1.1
50-99.9	4.8
100-499.9	5.9
≥500	1.1
	100.0%

Table 5. NUMBER OF MINERAL OIL TRANSFORMERS IN THE UTILITY INDUSTRY BY PCBs CONCENTRATION LEVEL (3).

Transformer Size (KVA rating)	Total Mineral Oil Transformers	Number of Transformers by PCBs Concentration in ppm					
		< 1	1-9.9	10-49.9	50-99.9	100-499.9	≥ 500
≤ 100	19,046,654	8,770,232	5,395,599	2,688,266	915,154	1,086,746	190,657
101-500	928,556	429,493	161,407	170,684	43,598	96,473	26,901
501-1,000	94,327	46,410	17,262	18,017	5,093	6,791	754
1,001-5,000	80,445	37,933	18,243	14,867	3,295	4,661	1,446
5,001-100,000	53,488	22,466	18,240	8,344	1,818	2,460	160
> 100,000	5,883	3,360	1,700	753	47	23	0
TOTAL	20,209,353	9,309,894	5,612,451	2,900,931	969,005	1,197,154	219,918

Table 6. PCBs CONCENTRATIONS BY TRANSFORMER SIZE (3).

Transformer Size (kVA Rating)	Percentage of Equipment Contaminated at PCBs Concentration (ppm) <1	1-9.9	10-49.9	50-99.9	100-499.9	≥500
≤100	46.1%	28.3%	14.1%	4.8%	5.7%	1.0%
101-500	46.2	17.4	18.4	4.7	10.4	2.9
501-1,000	49.2	18.3	19.1	5.4	7.2	0.8
1,001-5,000	47.1	22.7	18.5	4.1	5.8	1.8
5,001-100,000	42.0	34.1	15.6	3.4	4.6	0.3
>100,000	57.1	28.9	12.8	0.8	0.4	0.0

Table 7. PERCENT OF TRANSFORMERS CONTAINING LESS THAN 50 PPM PCBs (3).

Transformer Size (kVA rating)	% of Transformers with <50 ppm
≤100	88.4%
101-500	82.1
501-1,000	86.6
1,001-5,000	88.4
5,001-100,000	91.7
>100,000	98.8

Table 8. VOLUME OF FLUID CONTAINED IN MINERAL OIL TRANSFORMERS IN THE UTILITY INDUSTRY (3).

Transformer Size (kVA Rating)	Average Number of Gallons per Transformer	Total Number of Gallons of Mineral Oil
≤100	20	384,174,000
101-500	120	108,083,000
501-1,000	400	37,519,000
1,001-5,000	1,100	88,326,000
5,001-100,000	4,700	251,990,000
>100,000	15,000	88,273,000
		958,365,000

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The concentrations of PCBs in askarels vary from transformer to transformer. EPA has classified PCB transformers as follows:

1) > 500 ppm: includes all askarel-filled transformers and about 1.2% of all mineral oil transformers.

2) > 50 ppm but < 500 ppm: includes 8.8% of all mineral oil transformers.

3) < 50 ppm: includes 90% of all mineral oil transformers.

INSTALLATION AND POSSIBLE LOCATION OF TRANSFORMERS

The National Electrical Code (NEC) requires that mineral oil transformers located in or near buildings must be enclosed in vaults. Askarel transformers installed in similar locations must be enclosed in vaults only if they are rated at more than 35,000 volts. The NEC further provides specific construction requirements for vault walls, roof, floor, and doors. Vaults are typically constructed of concrete four to six inches thick.

If the transformer is to be vaulted, special provision must be made to ensure adequate heat release and cooling.

Possible locations of the transformer vary with many factors such as population of the building and the distribution network of the electric load. It is desirable to have the transformer away from crowded population to minimize fire hazard. The building design and the preference of the design engineer also weigh heavily in the location of the transformer. Most transformers can be found on the roof or in the basements of buildings, although some can be found outside or adjacent to the building on a pad or underground. A number are also found mounted on poles outside the buildings.

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SECTION 4

THE CHEMISTRY OF PCBs COMBUSTION

CHEMICAL CONSTITUENTS OF ASKARELS

Available information on the composition of askarels offers a rather hazy picture of the chemical constituents. In the last 60 years of commercial use, the formulation of askarels has undergone various changes and few manufacturers have made or kept records of the type and quality of PCBs and other chemical substances used in the formulating process. There is no evidence to indicate that in the early days, the PCBs and the diluents used to formulate askarels were required to meet particular chemical quality specifications. Performance specifications in terms of heat transfer properties were probably the only major requirements associated with the formulation process.

Askarel fluids are normally mixtures of 60% to 70% PCBs and 40% to 30% trichlorobenzenes. Chlorinated benzenes were added as solvents or diluents to improve the viscosity of PCBs for transformer fluids. Monsanto, the sole producer in the U.S., sold PCBs under the trade names of Aroclor 1242 (42% chlorine content), Aroclor 1254 (54% chlorine content) and Aroclor 1260 (60% chlorine content). The Aroclor mixture is referred to by a four digit number where the first two digits (i.e., 12) indicate the compound chlorobiphenyl and the last two digits represent the weight percent chlorine present in the mixture. Aroclor mixtures which General Electric has used in transformers have contained anywhere from 13% to 60% trichlorobenzene, with the remainder being pentachlorobiphenyl or hexachlorobiphenyl or mixtures of either tri-, penta-, or hexachlorobiphenyl and tetrachlorobenzene. The most common formulations of askarels used in the U.S. were Inerteen and Pyranol. Inerteen was used by Westinghouse and had at times contained 60% PCBs and 40% trichlorobenzenes. Pyranol was used by General Electric and contained 70% PCBs and 30% trichlorobenzenes. The exact compositions of both Inerteen and Pyranol were changed from time to time. Various isomers of PCBs and trichlorobenzenes along with other impurities were mixed in askarel fluids.

PCBs in Askarels

Theoretically, there are 209 possible PCBs isomers, although not all are found in manufactured products. Table 9 illustrates the possible isomers and the chlorine content of the PCBs class of chemicals.

Chlorobenzenes in Askarels

Chlorobenzenes are added to PCBs to alter the viscosity of the transformer fluid. Table 10 presents the isomers and their chlorine content. The trichloro- and tetrachlorobenzenes are the most common chlorobenzenes for askarels. The trichlorobenzenes in askarels are usually of a commercial grade and contain a mixture of isomers and other impurities. The trichlorobenzenes used by General Electric in dielectric fluid have the composition shown in Table 11.

Contaminants of Askarels

Small amounts of polychlorinated dibenzofurans (PCDFs) and polychlorinated naphthalenes (PCNs) have also been detected in PCBs mixtures. The quantities vary from batch to batch, reflecting production process variations. Bowes and coworkers (1) analyzed several samples of PCBs mixtures and found tetra-, penta-, and hexa-PCDFs at levels from 0.8 to 2 ppm, with levels up to 10 ppm for some European samples. They also detected 3 to 4 ppm of each hexa- and heptachloro-naphthalenes in Aroclor 1254. Miyata and Kashimoto (2) found 2 to 9 ppm PCDFs in Aroclor 1242 and 1260. No PCDDs are found in PCBs and askarel fluids. The finding of PCDDs at fire accident sites is mostly attributed to chemical reactions involving contaminants in askarel mixtures under thermal conditions.

PCBs COMBUSTION PROCESS CHARACTERISTICS

The major combustion products of PCBs are carbon dioxide, water and hydrochloric acid. Small amounts of other products known as Products of Incomplete Combustion (PICs) are also found in the combustion emissions.

Table 9. ISOMERS OF PCBs AND THEIR CHLORINE CONTENT.

Chlorobiphenyl	Molecular formula	Possible no. of isomers	Molecular weight	Weight % chlorine
mono -	$C_{12}H_9Cl$	3	188.65	18.79
di -	$C_{12}H_8Cl_2$	12	223.10	31.78
tri -	$C_{12}H_7Cl_3$	24	257.55	41.30
tetra -	$C_{12}H_6Cl_4$	42	291.99	48.57
penta -	$C_{12}H_5Cl_5$	46	326.44	54.30
hexa -	$C_{12}H_4Cl_6$	42	360.88	58.94
hepta -	$C_{12}H_3Cl_7$	24	395.33	62.78
octa -	$C_{12}H_2Cl_8$	12	429.77	65.99
nona -	$C_{12}HCl_9$	3	464.22	68.73
deca -	$C_{12}Cl_{10}$	1	498.66	71.10

Table 10. ISOMERS OF CHLOROBENZENES AND THEIR CHLORINE CONTENT.

Chlorobenzene	Formula	Molecular Weight	Weight % Chlorine	Number of Isomers
mono-	C_6H_5Cl	112.56	31.50	1
di-	$C_6H_4Cl_2$	147.00	48.24	3
tri-	$C_6H_3Cl_3$	181.45	58.62	3
tetra-	$C_6H_2Cl_4$	215.89	65.69	3
penta-	C_6HCl_5	250.34	70.81	1
hexa-	C_6Cl_6	284.78	74.70	1

Table 11. COMPOSITION OF GENERAL ELECTRIC'S DIELECTRIC GRADE TRICHLOROBENZENE.

1,2,4-Trichlorobenzene	> 70%
1,2,3-Trichlorobenzene and 1,3,5-Trichlorobenzene	> 20%
Dichlorobenzene	ca .1%
Tetrachlorobenzene	ca .1%
Pentachlorobenzene	trace

These PICs include the PCDFs, PCDDs and other toxic contaminants discussed earlier.

PICs are formed from the incomplete combustion of the reacting molecules in the incineration process. For instance, if 1000 gallons per hour of PCBs are being burned, 9×10^{27} molecules per hour of PCBs are undergoing reaction. If the probability of forming a particular incomplete combustion product was one in a trillion, then about 5 mcg per hour of that PIC would be produced. Characteristics of the feed that influence the formation of PICs include:

(1) the carbon-to-hydrogen ratio,

(2) the chlorine content, and

(3) the nature of the contaminants.

In general, the higher the carbon-to-hydrogen ratio, the greater the probability of forming PICs. Aromatic compounds have high carbon-to-hydrogen ratios and have a high probability for forming PICs when burned. The unsaturated ring is a stable building block and undergoes additional intermolecular reactions in a combustion zone to form more complex condensed ring structures.

Chlorine content of the PCBs is another important factor in the formation of PICs. Thermochemical calculations presented later show that the higher the chlorine content, the higher the concentrations of chlorinated PICs in the combustion products. The carbon-to-hydrogen ratio and the chlorine content for each PCB are listed in Table 12.

Process parameters also influence the formation of PICs in the combustion of PCBs. These parameters include:

(1) reaction (fire) temperature;

(2) residence time of reactants (air and fuel) and products in the high temperature zone;

(3) turbulence or mixing efficiency of fuel and air;

(4) air/fuel ratio including the effects of operating cycles on combustion air supply;

(5) fuel feed rate.

Table 12. CARBON/HYDROGEN RATIO AND CHLORINE CONTENT FOR PCBs.

Compound	C/H ratio (wt/wt)	Cl Content (wt%)
$C_{12}H_{10}$ (biphenyl, parent compound)	14.3	0.0
$C_{12}H_9Cl$	15.9	18.8
$C_{12}H_8Cl_2$	17.9	31.8
$C_{12}H_7Cl_3$	20.4	41.3
$C_{12}H_6Cl_4$	23.8	48.6
$C_{12}H_5Cl_5$	28.6	54.3
$C_{12}H_4Cl_6$	35.8	58.9
$C_{12}H_3Cl_7$	47.7	62.8
$C_{12}H_2Cl_8$	71.5	66.0
$C_{12}HCl_9$	143.0	68.7
$C_{12}Cl_{10}$	--	71.1

Laboratory studies have indicated that with adequate reaction time and efficient mixing between air and fuel, PCBs are completely decomposed into H_2O, CO_2, and HCl at a temperature range of 800-1000°C. Pyrolytic conditions, however, allow the formation of PCDFs. Duvall and Rubey (3, 4) investigated combustion efficiency under varying temperature conditions. They gradually vaporized PCBs samples into a flowing carrier gas, which were subsequently subjected to a controlled high temperature exposure in a quartz tube reactor. Compounds exiting from the high temperature zone were separated and analyzed by an in-line GC/MS. The results are shown in Tables 13 and 14.

Table 13. PERCENT OF PCBs REMAINING AFTER EXPOSURE AT DIFFERENT TEMPERATURES (3).

Compounds	Exposure Temperature (^{o}C)*						
	550	650	675	700	725	750	775
2,2′,5,5′-Tetrachlorobiphenyl	100	92	74	57	21	0.14	--
2,2′,4,5,5′-Pentachlorobiphenyl	100	98	80	53	9.3	0.05	0.007
2,2′,4,4′,5,5′-Hexachlorobiphenyl	100	100	73	26	--	--	0.005

* 2-second residence time, flowing air.

Table 14. PERCENT PCBs REMAINING AFTER TREATMENT AT 704°C (4).

Compound	Residence Time (sec in flowing air)		
	0.27	0.95	3.84
Biphenyl	8.1	0.7	0.07
2,2′,5,5′-Tetrachlorobiphenyl	78.5	14.0	2.6
2,2′,4,5,5′-Pentachlorobiphenyl	81.1	18.5	3.4
Decachlorobiphenyl	84.7	37.3	16.1

The data in Table 13 show that at a selected residence time, the decomposition efficiency of PCBs increases with exposure temperature. No decomposition of PCBs takes place below 550°C and PCBs only decompose moderately at temperatures between 650°-725°C. The data in Table 14 show that increased residence time results in increased decomposition of PCBs.

Using the data from Table 14, the decomposition rate of PCBs at 704°C is charted as shown in Figure 3. Extrapolation of data such as that presented in this section was utilized in developing the temperature and residence time guidelines for land-based incineration. PCBs burn tests at ENSCO facilities at El Dorado, Arkansas and at Rollins in Deer Park, Texas have confirmed PCBs destruction at the desired destruction efficiency when conducted within the specific guidelines.

THERMOCHEMICAL EQUILIBRIUM ANALYSIS OF PCDDs AND PCDFs FORMATION

The potential formation of polychlorinated dibenzofurans (PCDFs) and dibenzo-p-dioxins (PCDDs) during the combustion of PCBs can be predicted by thermochemical equilibrium calculations. However, accurate thermodynamic data are not available for PCDFs and PCDDs, and their formation potential may be examined only indirectly through review of combustion conditions and waste types that favor the formation of intermediates, such as chlorobenzenes and chlorophenols.

Shih, et al., calculated equilibrium products for several chlorinated wastes under pyrolytic conditions (5). These were theoretical equilibrium calculations and do not take reaction kinetics into account. The pyrolysis cases assumed the absence or near absence of oxygen and, hence, of oxidizing species. Such conditions may be encountered in a real combustion system in several ways:

- Malfunctions of cyclic operation leading to excessively lean air/fuel ratios,
- Poor mixing of fuel and air leading to localized oxygen deficient conditions,

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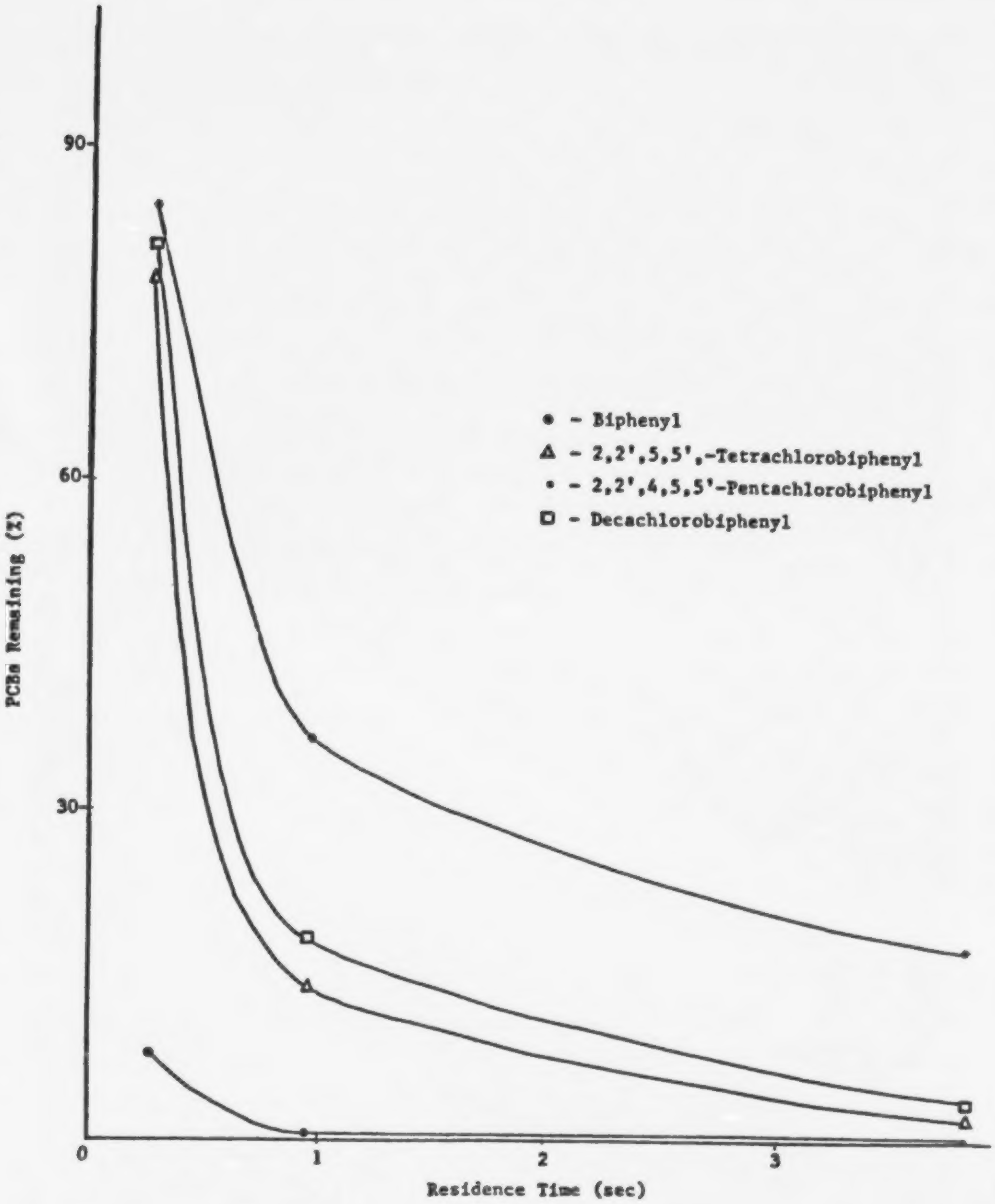

Figure 3. Decomposition of PCBs at 704°C

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- Thermal quenching of portions of the burning mixture at the walls and carrying of the quenched mixture into the hot post-flame region where pyrolysis can occur, and

- Pre-combustion reactions on the fuel side of the flame.

Shih's calculations cover a temperature range of 540°C (1000°F) to 1100°C (2000°F) for seven hypothetical wastes of varying carbon, hydrogen, and chlorine content. The program used was capable of simultaneously considering a maximum of 200 gaseous species, including alkenes, chlorinated benzenes, and chlorinated phenols. Calculations for the first three cases where the chlorine content is up to 10% led to the following observations (5):

- Under pyrolytic conditions, the major equilibrium products are: ethylene, acetylene, methane, benzene, styrene, monochlorobenzene, hydrogen, and hydrogen chloride.

- Concentrations of hydrochloric acid and monochlorobenzene increase with increasing chlorine content.

- Formation of ethylene, acetylene, and styrene is favored by increasing reaction temperatures.

- Formation of methane and toluene is favored by decreasing temperature.

- In the range studied, temperature appears to have a negligible effect on the formation of benzene, monochlorobenzene, and hydrochloric acid.

Calculations for mixtures containing from 50% to 73% chlorine led to the following observations:

- Major equilibrium products from pyrolysis of the highly chlorinated mixtures are: acetylene; benzene; styrene; mono-, di-, tri-, tetra-, penta-, and hexachlorobenzenes; hydrochloric acid in most cases; and carbon monoxide when small amounts of oxygen are present.

- Depending on the ratio of carbon-to-hydrogen-to-chlorine, hydrochloric acid is not necessarily favored by pyrolysis of highly chlorinated mixtures.

- Chlorobenzenes are more favored thermodynamically than chlorinated aliphatic and phenolic compounds.

- The relative equilibrium concentrations of polychlorinated benzenes generally increase with increasing chlorine content of the mixture.
- Reaction temperature in the range examined appears to have a negligible effect on the formation of hydrochloric acid and chlorobenzenes.
- The presence of small amounts of oxygen does not appear to have a major impact on the equilibrium product distribution except for the formation of carbon monoxide.

The second set of calculations indicated that, under pyrolytic conditions, formation of chlorobenzenes was thermodynamically feasible. Because chlorobenzenes are known precursors of PCDDs, PCDFs, and PCBs, these calculations under pyrolysis conditions implied that:

- PCDFs and PCDDs may form during the thermal destruction of PCBs carried out under pyrolytic conditions.
- PCDFs and PCDDs may form during thermal PCBs destruction carried out under oxidizing conditions in an incinerator if inadequate design and/or operation allow the existence of pyrolytic zones in the system.

The formation of PCDDs and PCDFs in PCBs have been attributed to the range of chemical reactions that occur in:

1) pyrolysis of PCBs,

2) condensation of chlorobenzenes, and

3) condensation of chlorophenols.

Both PCBs and chlorobenzenes are major components of PCB transformer fluid, whereas the chlorophenols are intermediates formed in the pyrolysis of chlorobenzenes. PCBs are also known to be contaminated with traces of PCDFs and polychlorinated naphthalenes (PCNs). These compounds are formed in the range of 550 to 700°C. The amounts of these compounds formed during the combustion process vary with temperature and concentration.

PCDDs AND PCDFs FROM PYROLYSIS OF PCBs

The pyrolysis of commercial PCBs yields about 30 major PCDFs and more than 30 minor PCDFs. One of the main constituents is 2,3,7,8-TCDF, potentially the most toxic of the PCDFs (7). The most toxic species are shown in Figure 4.

In a study by Buser, et al. (8), Aroclor 1254 was pyrolyzed at temperatures of 550°-750°C in quartz mini-ampoules. GC/MS analysis showed PCDFs were formed in the process. The results are presented in Table 15.

At 550-650°C, the decomposition at the 100 mcg-level ranged from 12% to 90%, at the 10 mcg-level it ranged from 80% to 98%. Aroclor 1254 was completely destroyed (> 99.9%) at temperatures of 700°C and above (see Figure 5).

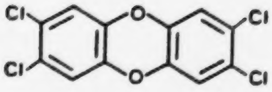
Table 15. PYROLYSIS OF AROCLOR 1254 IN QUARTZ MINI-AMPOULES (8).

Temp. (°C)	Amt. (mcg)	Decomp. (%)	PCDFs formed * (%)					
			mono-	di-	tri-	tetra-	penta-	Total
550	100	12	0.25	0.65	0.90	0.75	0.20	2.75
"	10	80	0.02	0.40	0.70	0.70	0.15	1.97
600	100	45	0.10	0.40	0.70	0.60	0.12	1.92
"	10	90	<0.01	0.10	0.25	0.35	0.05	<0.76
650	100	90	<0.01	0.02	0.18	0.25	0.12	<0.58
"	10	98	0.01	0.12	0.25	0.12	<0.02	<0.52
700	100	>99.9	<0.01	<0.01	<0.01	<0.02	<0.02	<0.07
"	10	>99.9	<0.01	<0.01	<0.01	<0.02	<0.02	<0.07
750	100	>99.9	<0.01	<0.01	<0.01	<0.02	<0.02	<0.07

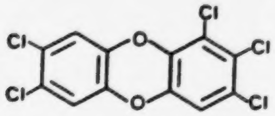
* Combined values of all isomers of a PCDF.

Mono- to penta-CDFs were found at temperatures of 550-650°C at levels ranging from < 0.01-0.90%. The maximum amounts found were at 550°C. Taking into consideration the amount of PCBs recovered after pyrolysis, the total yield of PCDFs ranged from 3-25% (see Figure 6).

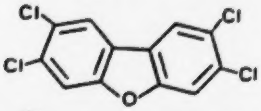
1. **2,3,7,8-Tetrachlorodibenzodioxin**



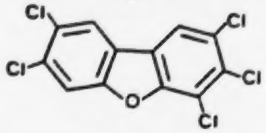
2. **1,2,3,7,8-Pentachlorodibenzodioxin**



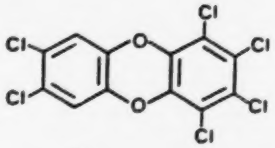
3. **2,3,7,8-Tetrachlorodibenzofuran**



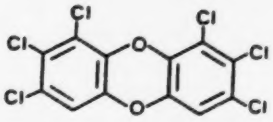
4. **2,3,4,7,8-Pentachlorodibenzofuran**



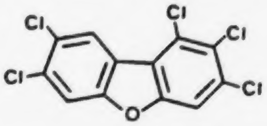
5. **1,2,3,4,7,8-Hexachlorodibenzodioxin**



6. **1,2,3,7,8,9-Hexachlorodibenzodioxin**



7. **1,2,3,7,8-Pentachlorodibenzofuran**



8. **1,2,3,6,7,8-Hexachlorodibenzodioxin**

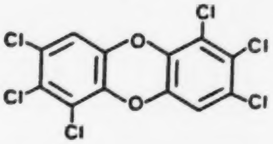


Figure 4. The Most Toxic PCDD and PCDF Isomers

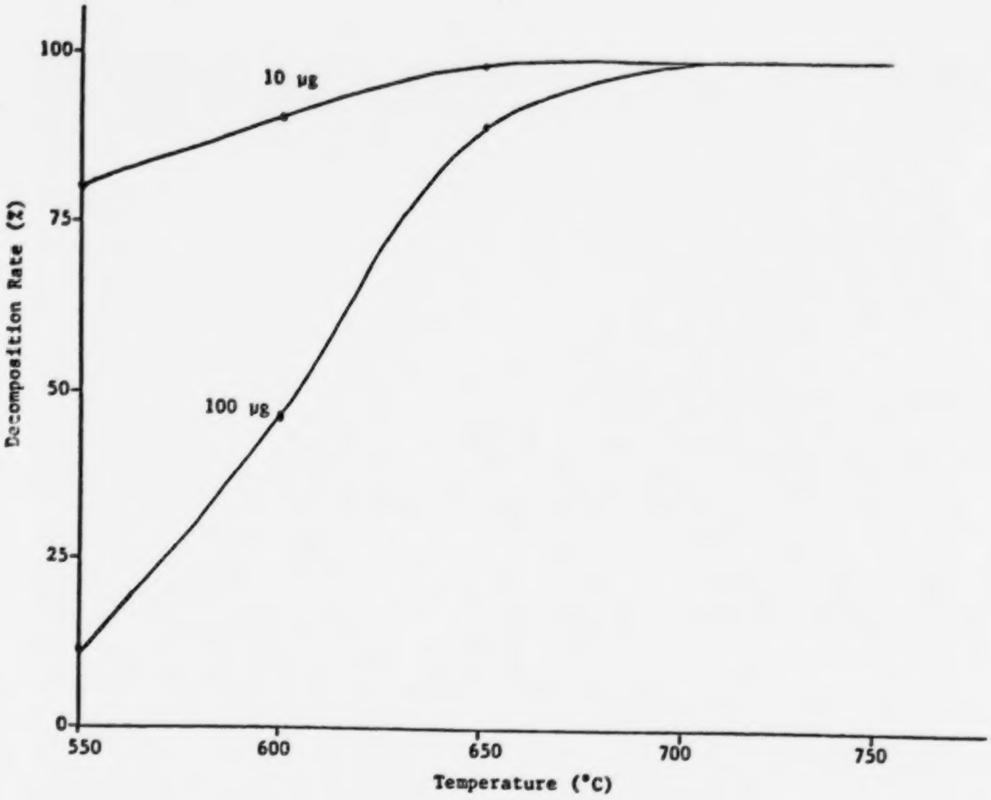


Figure 5. Pyrolysis of Aroclor 1254

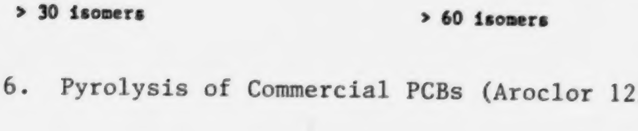

PCBs
PCDFs
Cl_x
600^oC
Cl_y
O
x = 1 - 8
> 30 isomers
y = 1 - 6 (yield 3-25%)
> 60 isomers

Figure 6. Pyrolysis of Commercial PCBs (Aroclor 1254, 1260)

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It was found that the cyclization process which yields PCDFs from PCBs was intermolecular and followed several competing reaction pathways (see Figure 7) (9, 10). In addition to PCDFs, polychlorinated biphenylols as possible precursors, were identified at levels of approximately one-fifth of the amount of PCDFs present.

Plots of the Aroclor 1254 decomposition rates and PCDFs formation vs. temperature ranges in the experiment are presented in Figure 5 and Figure 8. Because these values varied with the quantity of Aroclor 1254 used in the experiment, average values were also indicated.

There is no experimental evidence for PCDDs formation from pyrolysis of PCBs, and theoretical considerations indicate that this conversion does not occur.

FROM PYROLYSIS OF POLYCHLORINATED BENZENES

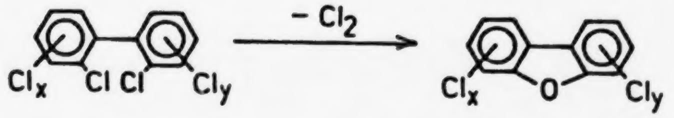
PCDDs and PCDFs are also produced from the pyrolysis of polychlorinated benzenes but the yields are lower than that from the pyrolysis of PCBs. In Buser's experiments using scaled quartz mini-ampoules (8), tetra- to octa-CDF and also tetra- to octa-CDD were identified in the pyrolysis of tri-, tetra- and pentachlorobenzenes. In addition to PCDFs and PCDDs, chlorophenols and a series of other chlorinated compounds were also formed.

Significant quantities of PCDFs and PCDDs were found in most of the pyrolyzed samples (see Tables 16 and 17). The formation of these tricyclic aromatic compounds is bimolecular; the likelihood of this formation is highly dependent on the concentration of chlorobenzenes in the reaction system (see Figure 9) (11). Figure 10 shows a possible reaction mechanism for dioxin formation from a trichlorobenzene (12).

As seen in Table 16, significant quantities of PCDFs were formed from the tri- and tetrachlorobenzenes and from the combined chlorobenzenes sample. Tetra-, penta- and hexa-CDF were formed from trichlorobenzenes, and hexa-, hepta- and octa-CDF were formed from tetrachlorobenzenes. The combined

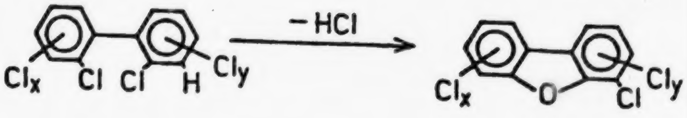
Reaction Route 1:

(loss of ortho - Cl_2)


Cl_x
Cl
Cl
Cl_y
$-Cl_2$
Cl_x
O
Cl_y

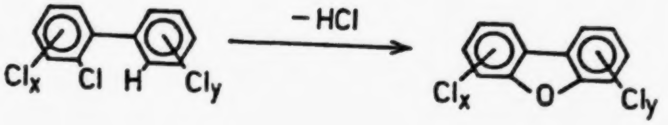
Reaction Route 2:

(loss of HCl involving a 2,3-chlorine shift)


Cl_x
Cl
Cl
H
Cl_y
$-HCl$
Cl_x
O
Cl
Cl_y

Reaction Route 3:

(loss of ortho - HCl)


Cl_x
Cl
H
Cl_y
$-HCl$
Cl_x
O
Cl_y

Reaction Route 4:

(loss of ortho - H_2)

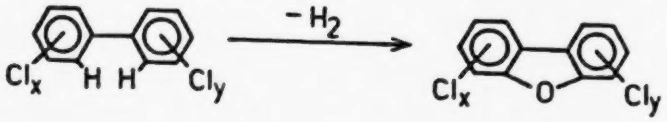

Cl_x
H
H
Cl_y
$-H_2$
Cl_x
O
Cl_y

Figure 7. Reaction Routes in the Pyrolysis of Individual PCBs (9)

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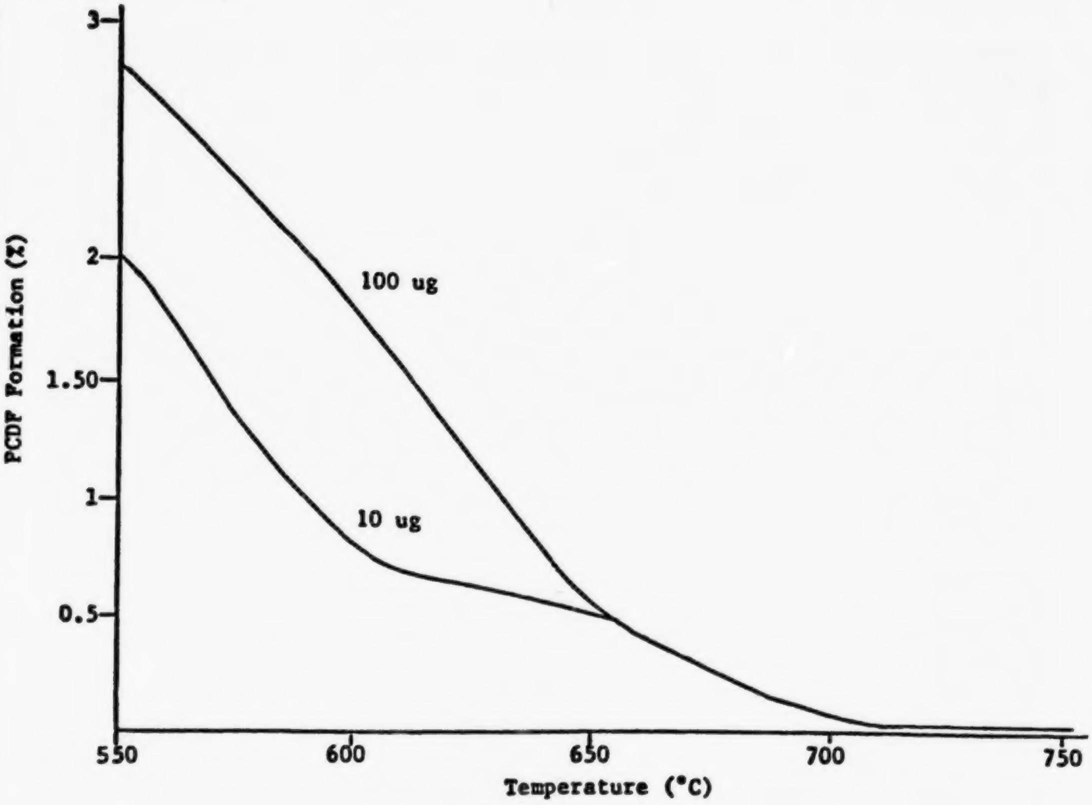

Figure 8. Pyrolysis of Aroclor 1254 and PCDF Formation

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Table 16. FORMATION OF PCDFs FROM THE PYROLYSIS OF CHLOROBENZENES (11).

	PCDFs formed (ng/sample)				
Compound(s)	tetra-	penta-	hexa-	hepta-	octa-
Trichlorobenzenes[a]	400	1100	550	50	< 5
Tetrachlorobenzenes[b]	< 2	5	160	450	200
Pentachlorobenzene[c]	< 2	< 5	< 5	5	30
Combined chlorobenzenes[d]	80	600	1100	600	60

a: 200 mcg total with equal amounts of 1,2,3-, 1,2,4- and 1,3,5-trichlorobenzene

b: 200 mcg total with equal amounts of 1,2,3,4-, 1,2,3,5- and 1,2,4,5-tetrachlorobenzene

c: 200 mcg pentachlorobenzene

d: 500 mcg total with equal amounts of all tri-, tetra- and pentachlorobenzenes (7 compounds).

Table 17. FORMATION OF PCDDs FROM THE PYROLYSIS OF CHLOROBENZENES (11).

	PCDDs formed (ng/sample)				
Compound(s)	tetra-	penta-	hexa-	hepta-	octa-
Trichlorobenzenes[a]	30	20	< 5	< 5	< 5
Tetrachlorobenzenes[b]	< 2	5	140	160	30
Pentachlorobenzene[c]	< 2	< 5	< 5	< 5	5
Combined chlorobenzenes[d]	50	220	220	70	5

a,b,c,d: for explanations see Table 16.

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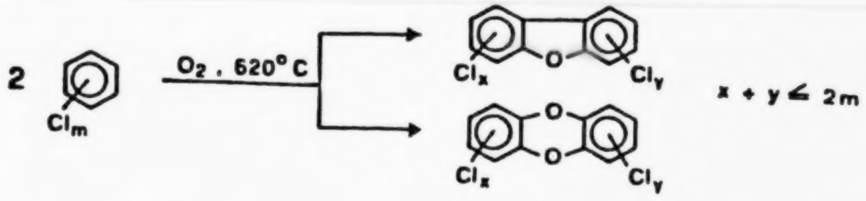
2
Cl_m
O_2, 620° C
Cl_x
Cl_y
O
x + y ≤ 2m

Figure 9. Formation of PCDFs and PCDDs from Polychlorinated Benzenes (10)

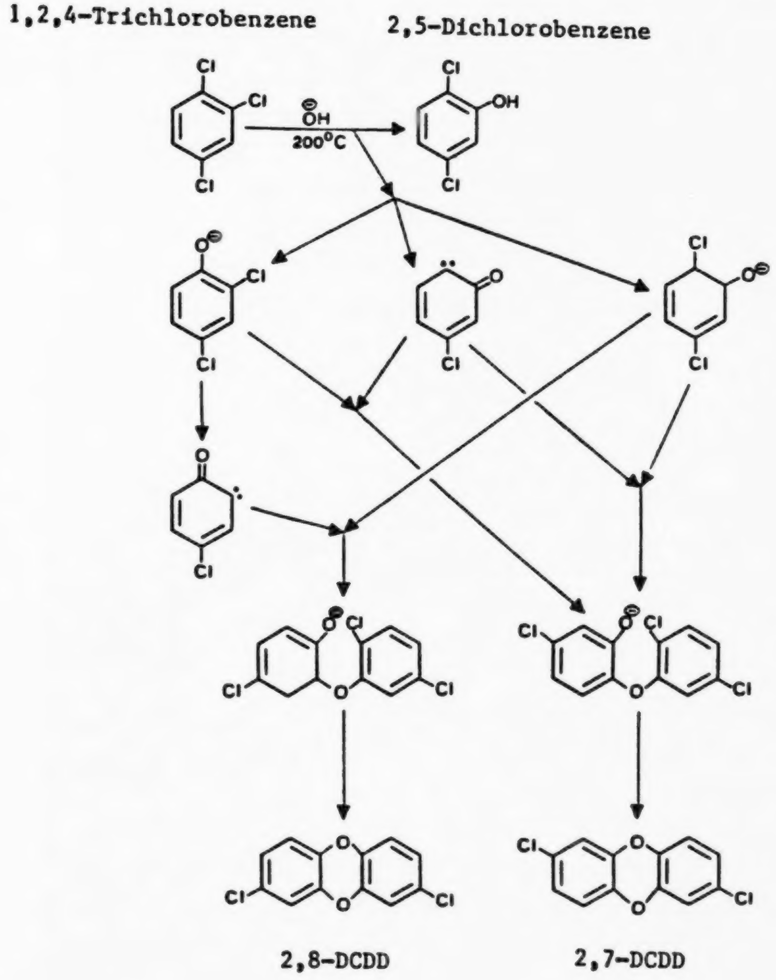
1,2,4-Trichlorobenzene
2,5-Dichlorobenzene
Cl
OH
OH
200°C
O
2,8-DCDD
2,7-DCDD

Figure 10. Proposed Reaction Mechanism for Dioxin Formation in the Production of 2,5-Dichlorophenol (11)

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sample formed PCDFs ranging from the tetra- to the octachloro compounds. In general, the PCDFs formed had chlorine numbers of 2m-2, 2m-1 and 2m, where m represents the chlorine number of the chlorobenzene employed. With the trichlorobenzenes, some higher chlorinated dibenzofurans (hepta-CDF) were also observed; presumably, they are formed from higher chlorinated benzenes produced during pyrolysis.

The optimal temperature for the conversion to PCDDs and PCDFs seems to be 500^{o}-600^{o}C. At temperatures exceeding 600^{o}-700^{o}C, the degradation of PCDDs and PCDFs takes place at a faster rate than the rate of formation. In addition to the temperature, the retention time is an important parameter.

The experimental results are summarized in Table 18. PCDDs and PCDFs isomers were present, but not as main components.

PCDDs AND PCDFs FROM PYROLYSIS OF CHLOROPHENOLS

Most of the commercial chlorophenols are contaminated with traces of PCDDs and PCDFs. Chlorophenols produced in chlorobenzenes pyrolysis form both PCDDs and PCDFs. Examples of PCDDs formation can be seen in Figure 11.

Table 18. FORMATION OF PCDDs AND PCDFs FROM THE PYROLYSIS OF CHLOROBENZENES (9).

	PCDDs	PCDFs
1,2,3-, 1,2,4- and 1,3,5-trichlorobenzene	0.025%	1%*
1,2,3,4-, 1,2,3,5- and 1,2,4,5-tetrachlorobenzene	0.15%	0.4%**
Pentachlorobenzene	0.002%	0.02%

* tetra-CDFs	0.2%	** hexa-CDFs	0.1%
penta-CDFs	0.5%	hepta-CDFs	0.2%
hexa-CDFs	0.3%	octa-CDF	0.2%

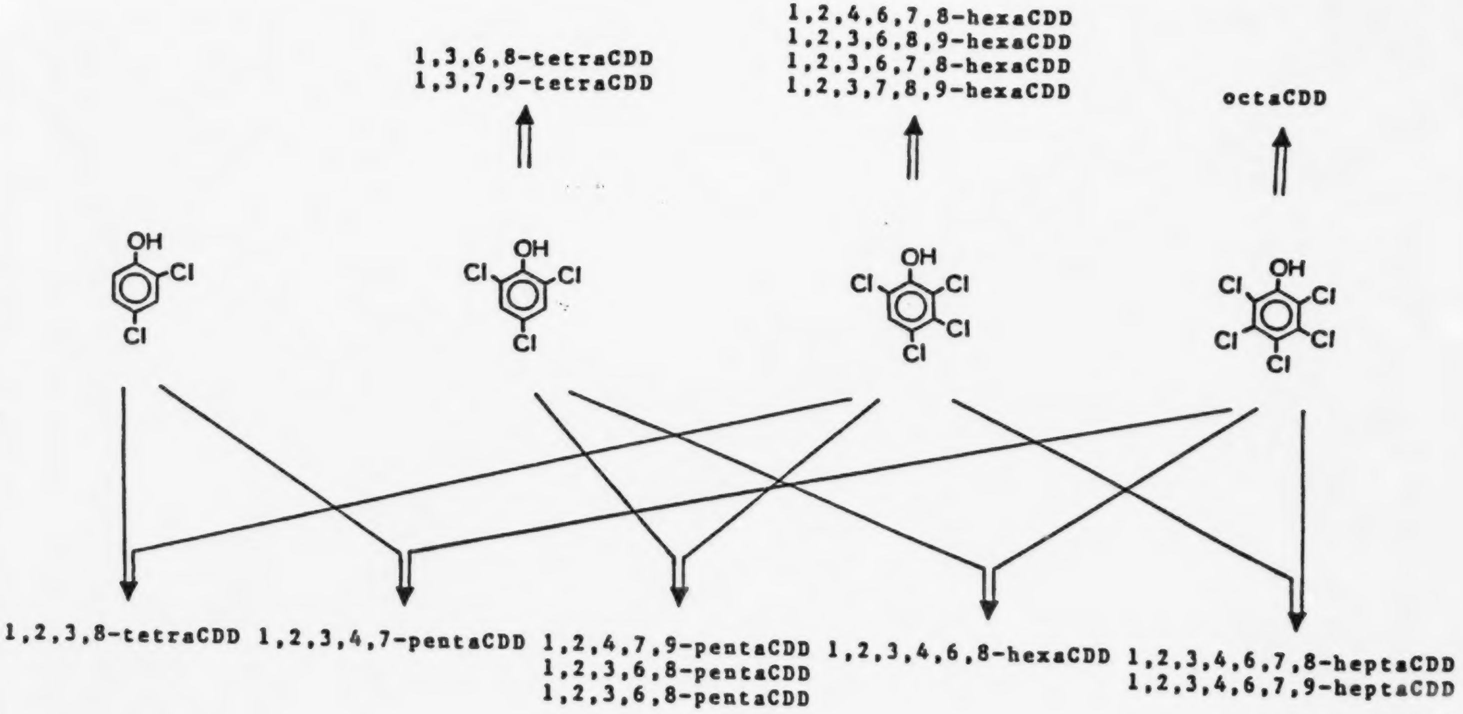
1,3,6,8-tetraCDD
1,3,7,9-tetraCDD
1,2,4,6,7,8-hexaCDD
1,2,3,6,8,9-hexaCDD
1,2,3,6,7,8-hexaCDD
1,2,3,7,8,9-hexaCDD
octaCDD
OH
Cl
Cl
1,2,3,8-tetraCDD
1,2,3,4,7-pentaCDD
1,2,4,7,9-pentaCDD
1,2,3,6,8-pentaCDD
1,2,3,6,8-pentaCDD
1,2,3,4,6,8-hexaCDD
1,2,3,4,6,7,8-heptaCDD
1,2,3,4,6,7,9-heptaCDD

Figure 11. PCDDs Formed Under Laboratory Pyrolysis of a Mixture of Common Commercial Chlorophenates (8)

Rappe, et al. (13), reported PCDDs and PCDFs formation from the burning of chlorophenols. Two of the most commonly used chlorophenol formulations on the Scandinavian market, Servarex Teknish (Gullviks Fabrinks AB, Malmo, Sweden, lot Npnr 524) and Kymmene KY-5 (Kymmene OY, Kuusankoski, Finland; lot 132/16), were used. These formulations contain approximately 5% of 2,4,6-tri-, 50% of 2,3,4,6-tetra- and 10% of pentachlorophenol in their sodium salt form. The levels of PCDDs found in the two formulations are similar (see Table 19), as were the levels of PCDFs.

Wood wool and birch leaves were impregnated with these formulations, ignited, and burned. The burning of the leaves proceeds slower and at a lower temperature with formation of more smoke and steam than the burning of the wood wool. Several individual burnings were carried out and the smoke gases were analyzed for PCDDs and PCDFs after adsorption on a charcoal or Amberlite XAD-2 filter.

In Table 19, the amounts of PCDDs found after the burning of impregnated wood wool and birch leaves are reported. It can be seen that the amounts of PCDDs increased and that PCDDs of all degrees of chlorination were formed.

The burning of impregnated birch leaves yielded similar amounts of PCDDs for both formulations when charcoal trapping was used. Somewhat lower values (yet not significantly lower) were found when using Amberlite XAD-2.

Samples of 2,4,6-trichlorophenol and pentachlorophenol of an isomeric purity of > 99% were prepared by multiple recrystallizations. The results from the burning of these purified 2,4,6-tri- and pentachlorophenate are given in Table 20. In these experiments, only birch leaves and charcoal filter trapping of the smoke gases were used. In the case of the 2,4,6-trichlorophenate, the dominating PCDDs were tetra-CDDs. In the case of the pentachlorophenate the highest level was found for the octa-CDD, but the amounts of hexa- and hepta-CDDs were found to exceed 50 mcg/g pentachlorophenate (13).

Table 19. AMOUNTS OF PCDDs FOUND IN BURNING EXPERIMENTS OF COMMERCIAL CHLOROPHENATES (13).

(mcg PCDDs/g chlorophenate)

	SERVAREX						KY-5	
		birch leaves			wood wool			birch leaves
	original sample	charcoal	ash	XAD-2	charcoal	XAD-2	original sample	charcoal
Tetra-CDDs	0.7	35	17	26	96	210	0.4	30
Penta-CDDs	5.2	90	58	59	120	357	3.5	84
Hexa-CDDs	9.5	80	74	57	110	347	5.3	82
Hepta-CDDs	5.6	8	18	8	65	29	2.1	8.2
Octa-CDD	0.7	0.3	6.4	0.2	1.2	1.2	0.3	0.4
TOTAL	21.7	213.3	173.4	150.2	392.2	944.2	11.6	204.6

Table 20. AMOUNTS OF PCDDs FOUND IN BURNING EXPERIMENTS OF PURIFIED CHLOROPHENATES (13).

(mcg PCDDs/g chlorophenate)

	2,4,6-Trichlorophenate		Pentachlorophenate	
	original sample	birch leaves charcoal	original sample	birch leaves charcoal
Tetra-CDDs	< 0.02	2100	< 0.02	5.2
Penta-CDDs	< 0.03	5.0	< 0.03	14
Hexa-CDDs	< 0.03	1.0	< 0.03	56
Hepta-CDDs	< 0.1	3.0	0.3	172
Octa-CDD	< 0.1	6.0	0.9	710
TOTAL	< 0.28	2115	1.28	957.2

PCDFs in Starting Materials and Burning Extracts

Using the same technique as previously described for the PCDDs, PCDFs in the starting materials and burning extracts were found. The main PCDFs in the starting materials were the hexa- and hepta-CDFs present at levels of 60-70 mcg/g each, and the amounts found for the tetra-, penta- and octa-CDFs were about 10 mcg/g. The same levels and the same isomers were found in the two formulations studied.

After burning, the levels of most PCDFs were generally lower (as opposed to PCDDs), but the levels of a few individual PCDFs nevertheless increased (e.g., the major tetra-CDF, an unknown isomer, increased during burning more than 100-fold from 0.04 to 5 mcg/g). Two PCDF isomers which increased upon burning had never been found in the starting material. 2,3,7,8-TCDF, which is considered to be the most toxic of all PCDFs, was only a minor component in all these samples and was less than 0.1% of the total tetra-CDFs in the starting material (7). The same PCDFs were formed in the Servarex micropyrolysis as in the burning experiments. However, no PCDFs could be found after the burning or micropyrolysis of the purified chlorophenates. Therefore, the PCDFs were formed from impurities in the chemical formulation, probably in reactions with higher absolute yields than those leading to PCDDs (13).

Test burns of pentachlorophenol (PCP) waste were performed in an industrial boiler in the U.S. Samples of baghouse ash and bottom ash were analyzed and results are reflected in Table 21. In the baghouse ash the total level of PCDDs was found to be 5.3 mcg/g. Lower chlorinated PCDDs predominated. In the bottom ash, the higher chlorinated PCDDs were found in greater amounts. PCDFs were found in the baghouse ash (14).

Table 21. LEVELS OF PCDDs AND PCDFs FROM BURNING OF PENTACHLOROPHENOL CONTAMINATED WASTE (mcg/g) (14).

Contaminant	Baghouse ash	Bottom ash
Tetra-CDDs	0.96	0.01
2,3,7,8-Tetra-CDD	<0.005	<0.001
Penta-CDDs	1.4	0.02
Hexa-CDDs	2.0	0.04
Hepta-CDDs	0.7	0.10
Octa-CDD	0.2	0.14
Tetra-CDFs	0.90	--
2,3,7,8-Tetra-CDF	0.10	--
Penta-CDFs	1.5	--
1,2,3,7,8-Penta-CDF	0.05	--
2,3,4,7,8-Penta-CDF	0.10	--
Hexa-CDFs	0.15	--
1,2,3,4,7,8-Hexa-CDF	0.02	--
Hepta-CDFs	0.06	--
Octa-CDF	0.006	--

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SECTION 5

PCBs FIRE INCIDENTS

ANALYSIS FOR PCBs, PCDDs AND PCDFs AT FIRE ACCIDENT SITES

The analysis of soot samples from actual PCBs incidents has led to concern for the safety of fire fighter personnel and the importance of clean-up measures.

In this section the results of sample analysis for PCBs, PCDDs and PCDFs are presented from the following fires:

- Norrtalje, Sweden
- Cincinnati, Ohio
- Binghamton, New York
- Stockholm, Sweden
- Boston, Massachusetts
- Skovde, Sweden
- Miami, Florida
- St. Paul, Minnesota
- San Francisco, California
- Other Fires.

Norrtalje, Sweden

On September 25, 1978 there was an intense fire in a capacitor battery north of Norrtalje, Sweden. The fire could not be extinguished for over thirty minutes while high voltages were turned off. Eighteen PCBs-containing capacitors (100 kVA each) were involved in the fire. When the capacitors were demounted, some showed no signs of damage while others had exploded with the contents exposed. B. Jansson and G. Sundstrom (1) at the Special Analytical Laboratory, National Swedish Environmental Protection Board located at the University of Stockholm were contacted a few weeks after the accident and asked to perform sample analysis for PCDFs formation. Up to 300 mg samples together with 100 ng [2,3,7,8-^{37}Cl]-tetrachloro-[1,4,6,9-^{2}H]-dibenzo-p-dioxin as internal standard dissolved in 1 ml n-hexane were chromatographed on aluminum oxide. The first fraction containing most of the PCBs was eluted with 90 ml 5% dichloromethane in n-hexane. The second fraction which was eluted with 60 ml dichloromethane contained all PCDF references, the internal standard and at least two PCBs.

Results of the analysis are given in Table 22. An Aroclor 1242 standard was used as a reference. Samples were taken from intact and exploded capacitors, from the wire fence surrounding the capacitors (fence was washed with acetone to obtain sample), and from pinetree needles which were located about 10 m downwind from the fire.

Table 22. PCB AND PCDF LEVELS IN CAPACITORS AND IN ENVIRONMENTAL SAMPLES (1).

Sample	PCB[a] g/g sample	PCDF mcg/g sample					PCDF/PCB mcg/g
		mono-CDF	di-CDF	tri-CDF	tetra-CDF	PCDF	
Liquid in intact capacitor	0.83-0.86	0.2-0.5	0.2	0.2-0.3	0.2-0.3	0.9-1.1	1.1-1.3
Liquid in exploded capacitor	0.93	24	38	11	3	75	81
Liquid on exploded capacitor	0.49-0.60	12-21	9-21	3-7	2	27-52	45-107
Extract from wire fence	0.3×10^{-3}	<0.03	<0.2	<0.03	<0.04	<0.3	-
Pine needles	0.3×10^{-6}	n.d.	n.d.	n.d.	n.d.	n.d.	-

[a] as Aroclor 1242

The wire fence was found to contain unexpectedly low PCB concentrations. The extractable part contained only 0.3 mg PCB per g extractables. As a result of this low PCBs level the upper limit of the PCDF/PCB ratio for the fence extract becomes high. While no presence of PCDF was found in the fence sample, if the extremely high detection limit for the dichlorinated compounds is excluded, the highest possible concentration should be about 300 mcg per g PCBs.

In addition to these environmental samples, blood samples were taken from 6 firemen who were exposed to the fire. The samples were not taken until a few weeks after the fire incident. At that time the PCB levels in the blood samples were within the same range 2.3 to 3.6 mg PCBs/g as those for unexposed Swedes (1).

Cincinnati, Ohio

On December 3, 1980, a capacitor containing PCBs for an electric motor in a unit heater overheated in a basement storage room of Our Lady of Visitation Elementary School in Cincinnati, Ohio (2). The capacitor was used for a one-half horsepower electric motor in the unit heater. The motor's capacitor contained a design specification dielectric fluid volume of 22 ml, of which 99.6% by volume (or 21.91 ml) was a biodegradable fluid and 0.4% by volume (or 0.088 ml) was PCBs (Aroclor 1254). On March 18, 1981, NIOSH was requested by the Hamilton County Health Department to determine the extent of PCBs contamination of the school. Air and surface wipe samples were obtained throughout the school building on March 19 and 26 to determine the presence of PCBs.

Airborne PCBs were collected on Florisil packed in approximately 7 cm long 4 mm I.D. glass tubes. The Florisil was packed into two sections separated by a polyurethane plug: the front section contained 100 mg and the backup section (used as the blank) contained 50 mg of Florisil. The samples were collected using calibrated constant flow vacuum pumps operating at 0.20 liters per minute. The PCBs were desorbed from the Florisil with toluene and analyzed using a gas chromatograph equipped with an electron capture detector. Air concentrations were reported as micrograms (mcg) of PCBs per cubic meter (m^3) of air sampled. As seen in Table 23, PCBs were not detected in air samples obtained in the basement storage room nor in another room tested. These results were as expected based on the extremely low vaporization rate (0.000052 g/cm^2/hr at 100°C) of Aroclor 1254.

Wipe samples of surfaces were obtained by wiping an area of approximately 100 cm^2 using a Whatman smear tab moistened with pesticide quality cyclohexane. The samples were extracted using toluene and analyzed using the procedure used for the air samples. The presence of PCBs was reported as mcg per 100 cm^2 of surface area. As seen in Table 24, samples obtained from the floor, ceiling, desk and bookshelves in the basement storage room (Room 27) showed a surface presence of < 0.05 to 7200 mcg PCBs/100 cm^2 (5-72,000 mcg/m^2). Background levels of PCBs on surfaces in the school showed a presence of < 0.05 to 0.45 mcg PCBs/100 cm^2. Surfaces tested in buildings in eastern, central and western Cincinnati showed a background presence of < 0.05 to 0.13 mcg/100 cm^2 ($\leq$ 5-13 mcg/m^2).

The two wipe samples with the highest concentration of PCBs were also analyzed for PCDDs and PCDFs with special emphasis on the 2,3,7,8-isomers. No dibenzodioxins or dibenzofurans were detected in either of the samples. The lower limits of analytical detection using this method were 0.10 and 0.09 mcg/100 cm^2 sample, respectively.

The Health Commissioner of Hamilton County offered the following recommendations to the school:

1. The concentration of PCBs on surfaces (i.e., floor, desks, bookshelves) in Room 27 should be reduced to background levels, i.e., less than 0.5 mcg PCBs/100 cm^2 surface area (50 mcg/m^2).
2. Other than Room 27 no rooms require decontamination.

The school was reopened in all areas except the wing containing the contaminated storage Room 27 and nearby classrooms 24, 25 and 26 (2).

Table 23. ANALYSIS OF PCBs IN AIR SAMPLES FROM SCHOOL IN OHIO (2).

Sample Location	Volume (L)	Air Sample Levels
Inside heating unit on floor (Room 27)	45.2	N.D.*
Center of room on bookshelf	43.3	N.D.
Principal's office	34.7	N.D.

* N.D. or None Detected means that the PCBs were not detected at the lowest level (< 0.05 mcg/sample) capable of being measured by the analytical method equivalent to an airborne concentration of approximately < 1 mcg/m^3 for these samples.

Table 24. SUMMARY OF PCBs* WIPE SAMPLE RESULTS FROM SCHOOL IN OHIO (2).

		PCBs Level (mcg/100 cm^2)	
Sample Location	n	Mean	Range
Room 27 (Basement location)	20	771	< 0.05-7200 **
Room 25	4	0.08	< 0.05-0.14
Room 24	3	0.05	< 0.05-0.06 ***
Room 26	3	< 0.05	< 0.05 ****
Hallway between rooms 24-27	4	0.05	< 0.05-0.07
Room 8	4	0.06	< 0.05-0.08
Room 22	6	0.11	< 0.05-0.29
Room 9	2	0.11	< 0.05-0.16
Room 10	4	0.12	< 0.05-0.20
Room 11	2	0.09	< 0.07-0.11
Room 12	2	0.08	< 0.06-0.09
A.V. room	4	< 0.05	< 0.05
Principal's office	3	0.21	0.05-0.45
Mobile classroom	2	0.06	0.06
Background level (3 locations)	10	0.07	< 0.05-0.13

* Reported as Aroclor 1254.

** A < value means PCBs were not detected at detection limit.

*** Excludes sample taken on capacitor surface showing PCBs presence of 4.9 mcg/100 cm^2.

**** Excludes sample taken on capacitor surface showing PCBs presence of 2.3 mcg/100 cm^2.

n = number of samples

Rooms 27, 25, 26 and 24 were all in the basement.

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Binghamton, New York

On February 5, 1981, a fire broke out in the basement of the State Office Building in Binghamton, New York. In this fire, electrical arcing from a nearby switchgear ignited insulation around a basement transformer. A number of explosions were heard from the machine room and, before the electrical power could be switched off, it was obvious that the fire had affected the transformer. Approximately 180 gallons of Pyranol (65% Aroclor 1254 and 35% polychlorinated benzenes) had been lost from the transformer. The floor of the machine room was covered with an oily substance with a strong smell. The electric company informed the Assistant Fire Chief that the transformer contained PCBs. After additional calls by the Assistant Fire Chief to CHEMTREC and EPA, information was gained on how to protect fire fighting personnel from further exposure. The initial exposure to the Pyranol and heavy smoke had already caused reactions in a number of fire fighting personnel ranging from acute nausea to skin rashes, high liver enzymes, high cholesterol and triglyceride levels, to respiratory problems. Over 1 billion dollars in lawsuits have been filed in the names of 23 individuals and groups against the state. Most of the claims have been filed by the fire fighters. Some 500 people who believe they were exposed are being monitored (3, 4).

The New York Office of General Services began an immediate clean-up of the building. Members of the clean-up crew also developed skin rashes and on February 26, clean-up was halted when the actual levels of PCDFs and PCDDs were discovered. Ten different pentachlorinated dibenzofurans were identified. PCBs, 2,3,7,8-TCDD, and 2,3,7,8-TCDF were found throughout the building. Results are summarized in Tables 25 and 26. The total PCDF concentrations in the soot were initially found to be as high as 2163 mcg/g, PCDDs 10-20 mcg/g, and PCBs 100,000-200,000 mcg/g (3, 5, 6, 7, 8).

Table 27 lists the levels of PCDFs in the soot samples collected from each of the 17 floors of the State Office Building. The samples were taken by wiping one half (2 ft x 2 ft) of a ceiling panel with dry cellulosic filter paper. The particles were extracted with benzene and concentrated. The samples were spiked with ^{13}C 2,3,7,8-TCDD, ^{37}Cl TCDF and ^{37}Cl OCDD. Each

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Table 25. AMOUNTS OF PCBs, PCDDs, PCDFs FOUND AT BINGHAMTON STATE OFFICE BUILDING PRIOR TO CLEAN-UP (5, 7).

Sample Location	Type of Sample	Chemical	Amount (Average)
Composite (throughout building)	Air	PCBs	1.48 mcg/m^3
Composite	Air	2,3,7,8-TCDD	0.3 ppm
Composite	Air	2,3,7,8-TCDF	21 ppm
Composite	Soot	2,3,7,8-TCDD	3.5 ppm
Composite	Soot	2,3,7,8-TCDF	200 ppm
4th and 7th floor	Soot	2,3,7,8-TCDD	2-5 mcg/g
4th and 7th floor	Soot	2,3,7,8-TCDF	300 mcg/g
Air ducts	Soot	PCBs	156-1200 mcg/m^2
Interstitial space above ceiling levels	Soot	PCBs	1995 mcg/m^2
Exposed horizontal surfaces (desk tops, floors, sills)	Soot	PCBs	162.18 mcg/m^2
Exposed vertical surfaces (walls, desk sides)	Soot	PCBs	6.76 mcg/m^2
Unexposed horizontal surfaces (inside closed file cabinets and desk drawers)	Soot	PCBs	74.47 mcg/m^2
Unexposed vertical surfaces (inside closed cabinets and drawers)	Soot	PCBs	4.62 mcg/m^2
Garage and sub-basement floors and surface areas	Soot (swab)	PCBs	0.61 mcg/m^2

Table 26. LEVELS OF PCDFs AND PCDDs IN SOOT FROM ACCIDENTAL BURNING OF PCBs-CONTAINING ELECTRICAL EQUIPMENT AT BINGHAMTON (6, 8).

Isomers	Amount (mcg/g)
Total PCDFs	2163
Total Tri-CDFs	--
Total Tetra-CDFs	28
2,3,7,8-Tetra-CDF	12
Other Tetra-CDF Isomers (6)	16
Total Penta-CDFs	670
1,3,4,7,8-Penta-CDF	65
1,2,4,7,8-Penta-CDF	25
1,2,4,7,9-Penta-CDF	22
1,2,3,7,8-Penta-CDF	310
1,2,3,6,7-Penta-CDF	60
1,2,6,7,8-Penta-CDF	25
2,3,4,7,8-Penta-CDF	48
2,3,4,6,7-Penta-CDF	12
Other Penta-CDF Isomers (12)	110
Total Hexa-CDFs	965
1,2,3,4,6,8-Hexa-CDF	50
1,3,4,6,7,8-Hexa-CDF	125
1,2,4,6,7,8-Hexa-CDF	50
1,2,3,4,7,8-Hexa-CDF	510
1,2,3,6,7,8-Hexa-CDF	150
1,2,3,6,8,9-Hexa-CDF	58
2,3,4,6,7,8-Hexa-CDF	10
Other Hexa-CDF Isomers	250
Total Hepta-CDFs	460
1,2,3,4,6,7,8-Hepta-CDF	230
1,2,3,4,6,7,9-Hepta-CDF	120
1,2,3,4,6,8,9-Hepta-CDF	55
1,2,3,4,7,8,9-Hepta-CDF	55
Octa-CDF	40
Total PCDDs	20
Total Tri-CDDs	--
Total Tetra-CDDs	1.2
2,3,7,8-Tetra-CDD	0.6
Other Tetra-CDD Isomers (4)	0.6

Table 26. (Continued)

Isomers	Amount (mcg/g)
Total Penta-CDDs	5.0
1,2,3,7,8-Penta-CDD	2.5
Other Penta-CDD Isomers (7)	2.5
Total Hexa-CDDs	4.7
1,2,3,4,6,8-Hexa-CDD	1.2
1,2,4,6,8,9-Hexa-CDD	1.2
1,2,3,4,7,8-Hexa-CDD	0.7
1,2,3,6,8,9-Hexa-CDD	0.6
1,2,3,7,8,9-Hexa-CDD	0.4
1,2,3,4,6,7-Hexa-CDD	0.5
Total Hepta-CDDs	7
1,2,3,4,6,7,9-Hepta-CDD	4
1,2,3,4,6,7,8-Hepta-CDD	3
Octa-CDD	2

Table 27. CONCENTRATION (mcg/g) OF PCDFs IN SOOT SAMPLES TAKEN FROM THE BINGHAMTON STATE OFFICE BUILDING (9).

Floor #	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
PCDFs[3]																	
Tetra-CDF	0.06		1.8	2.5	44	5.1	77	35	160	47	150	0.7	.97	9.9	84	(2)	139
^{37}Cl Tetra-CDF(ng)[1]	10.7ng		3.8ng	7.2ng	4.4ng	8.6ng	14.2ng	9.6ng	1.9ng	6.5ng	30.2ng	0.15ng	2.8ng	12.1ng	4.8ng		25.3ng
Penta-CDF	<0.06		<2.0	3.2	55	8.0	75	40	220	55	210	27	5.2	9.7	88	149	159
Hexa-CDF	<0.07		<2.4	2.0	36	3.0	14	16	140	28	160	42	4.3	—	16	89	86
Hepta-CDF	<0.08		<2.8	0.2	12	0.6	1.5	7.1	51	2.1	57	12	<2.0	1.8	20	34	20
Octa-CDF	<0.09		<3.1	<0.2	4.2	<0.2	—	1.4	17	0.56	18	3.6	<2.0	0.86	4.7	11	9.3
[4]Recovery	29		22	16	20	22	41	50	49	33	59	<1	7	31	28	—	62

[1] Internal standard amount recovered (ng)

[2] Data lost due to instrument malfunction

[3] Data uncorrected for recovery

[4] Recovery based on ^{37}Cl Tetra-CDF internal standard

sample was diluted with acetone to 20% benzene, applied to a low pressure LC system (PX-21 adsorptive carbon/celite), and washed with 40 ml 20% benzene/acetone. Flow through the column was reversed and the PCDDs/PCDFs fraction was eluted with 30 ml toluene. This fraction was condensed and redissolved in dodecane, applied to a 2% deactivated silica gel column and eluted with hexane. The eluted sample was then applied to an activated Florisil column and washed with 20 ml benzene to remove PCBs. PCDDs/PCDFs were eluted with 20 ml of 3% cyanomethane 47% dichloromethane and 50% hexane. The sample was concentrated in benzene before GC/HRMS analysis (9).

The entire 18 story building has been abandoned awaiting clean-up. Clean-up is expected to cost 2 or 3 times the building's original cost. Clean-up efforts have begun at a slow pace. On the advice of expert consultants, 3 contracts have been issued. These include:

1) Air Pollution Control Systems Contract

   - purchase and installation of air pollution control equipment on the roof including fans, chemical and particulate filters and necessary duct work.

2) Entry Module Contract

   - purchase of a partially outfitted mobile structure which was expanded and modified to include temporary entry facilities and locker areas, rest rooms, and security offices so that complete control of entry could be maintained.

3) Preliminary Clean-up Contract

   - intended to accomplish removal of soot. This operation includes high efficiency vacuum cleaning, wiping and washing of exposed surfaces and readily accessible hidden areas, removal of files, records, furniture and personal effects.

The site is expected to remain vacant for several years while undergoing decontamination procedures. Ongoing activities related to the site, program and overall management of current activities include:

1. Program organization
2. Security

3. Contaminant control
4. Emergency response
5. Support of community resources
6. Control of water discharged from site
7. Control of air movements
8. Planning for solid waste disposal
9. Disposal of contaminated documents
10. Collection of soot samples
11. Air sampling in the garage of site complex.

Stockholm, Sweden

In August 1981, an explosion (electrical arc) took place in a 10 kv capacitor battery in an electrical power station in Stockholm, Sweden. Kleenex tissue wipe tests (assumably 1 dm^2) were taken about 1 m from the capacitor and were tested for PCDF and PCDD levels. Extraction and measurement was accomplished by spiking the wipe tests with 1-5 ng of labeled CDD. The sample was treated with 10 ml of 1M HCl for 1 hr. The slurry was filtered and dried, extracted with toluene and dried with N_2. The residues were redissolved in 2 ml of n-hexane, added to a silica gel column and eluted with 5 ml of n-hexane. The hexane was evaporated with N_2 until 10 mcl remained. PCDDs and PCDFs were separated from other polychlorinated impurities using an Alox-column. The first fraction, 10 ml n-hexane:methylene chloride (98:2) was discharged. The second fraction, 10 ml n-hexane:methylene chloride (1:1) was collected and dried in N_2. This residue was used in the GC/MS analyses. Individual MS-response factors were used to calculate levels given in Table 28. Roughly 25-30 mcg/m^2 polychlorinated biphenylenes (PCBPs) were also found (8, 10). Polychlorinated pyrenes (PCPYs) were also detected but not quantified.

Table 28. AMOUNTS OF PCDFs FOUND IN SAMPLES FROM ACCIDENTAL PCB FIRE, STOCKHOLM, SWEDEN (8, 10).

PCDF	Amount (ng/m^2)
2,3,7,8-Tetra-CDF	150
1,2,7,8-Tetra-CDF	150
2,3,6,8-Tetra-CDF	125
1,4,6,9-Tetra-CDF	75
2,4,6,7-Tetra-CDF	37
3,4,5,7-Tetra-CDF	7.5
1,3,6,7- and 1,3,6,9-Tetra-CDF	300
Other Tetra-CDFs	750
Total Tetra-CDFs	1200
2,3,4,7,8-Penta-CDF	45
1,2,4,7,8-Penta-CDF	38
1,2,3,6,7-Penta-CDF	15
1,3,4,7,8-Penta-CDF	11
2,3,4,6,7-Penta-CDF	7.5
1,2,4,6,8-Penta-CDF	3.8
1,2,4,7,8-Penta-CDF	3.8
1,2,3,6,7-Penta-CDF	3.8
1,2,4,8,9-Penta-CDF	3.8
2,3,4,6,8-Penta-CDF	2
1,2,3,7,8- and 1,2,3,4,8-Penta-CDF	15
Other Penta-CDFs	19
Total Penta-CDFs	175
Total Hexa-CDFs	< 0.5

Boston, Massachusetts

In January 1982, an electrical fire involving a transformer containing Aroclor 1254 occurred in a Region I OSHA Department of Labor facility in Boston, Massachusetts. One bulk soot sample was analyzed for the presence of PCDDs and PCDFs. The bulk soot sample was spiked with 200 ng d_{12}-chrysene and was then Soxhlet extracted for 24 hours with hot toluene. This extract was decanted and labelled fraction 1. More hot toluene was added to the sample for an additional 24 hours. The extract was labelled fraction 2. Both extracts were analyzed. 70% of the d_{12}-chrysene was recovered in fraction 1. The two extracts were concentrated. Fraction 1 required multiple HRGC-MS analysis because of its complex components. PCDFs were confirmed in fraction 1. These results are shown in Table 29 (11).

Table 29. LEVELS OF PCDFs AND PCDDs FROM ACCIDENTAL BURNING OF PCBs-CONTAINING ELECTRICAL EQUIPMENT AT BOSTON, MASSACHUSETTS (11).

Isomers	Concentration mcg/g Soot
Total PCDFs	165
Total Tri-CDFs	50
Total Tetra-CDFs	60
2,3,7,8-Tetra-CDF	3
Total Penta-CDFs	35
Total Hexa-CDFs	15
Total Hepta-CDFs	2
Octa-CDF	n.d.
Total PCDDs	n.d.
Total Tri-CDDs	n.d.
Total Tetra-CDDs	n.d.
2,3,7,8-Tetra-CDD	n.d.
Total Penta-CDDs	n.d.
Total Hexa-CDDs	n.d.
1,2,3,4,6,7,9-Hepta-CDD	n.d.
1,2,3,4,6,7,8-Hepta-CDD	n.d.
Octa-CDD	n.d.

*Detection limit: 100 ng/g = 0.1 mcg/g = 0.1 ppm

Skovde, Sweden

In March 1982, a fire broke out in a capacitor battery serving a high-frequency oven in a metal treatment factory in Skovde, Sweden. Both mineral oil and PCBs types of capacitors were in use. There were no chlorinated benzene additives in the oil. The fire started in a mineral oil capacitor and 2 hours elapsed until the fire was extinguished. The smoke spread to an extent of 60 m x 30 m. Copper bars for electricity in the capacitor room ceiling partially melted (m.p. 1080°C). The capacitor battery contained 21 capacitors filled with PCBs (5 kg each). After the fire, 12 of these capacitors had been opened, 9 remained sealed.

Wipe tests (tissue 1 dm^2) were used to take samples from a) floor of capacitor battery, b) floor close to battery, c) the wall of the capacitor room, 2 m from the battery, 3 m above the floor, and d) bench 10 m from the oven (1 floor above the capacitor). Table 30 shows the results. High levels of PCDFs could only be found close to the fire. No PCDDs or polychlorinated biphenylenes (PCBPs) could be identified in the samples from this fire (8, 10).

Miami, Florida

On April 13, 1982, a fire involving an underground electrical transformer vault occurred in Miami, Florida (12). The International Association of Fire Fighters (I.A.F.F.) requested NIOSH to perform analyses of surface samples in order to determine if fire fighters had been exposed to PCBs or other more toxic decomposition products such as PCDDs and PCDFs. The fire fighters were also concerned about the possible contamination of fire equipment and protective clothing used during the fire.

In these analyses, samples were collected by NIOSH in two ways. Swipe samples were collected using sterile cotton pads saturated with n-hexane from sample areas with an approximate size of 100 cm^2. Surfaces thought to be less heavily contaminated were wiped with dry Whatman smear tabs.

Table 30. LEVELS OF PCDFs (ng/m^2) FOR SAMPLES FROM THE SKOVDE FIRE (8, 10).

	Sample Number			
	a	b	c	d
2,3,7,8-Tetra-CDF	20	100	< 1	n.d.
Total Tetra-CDFs	100	600	< 1	10*
Total Penta-CDFs	40	100	n.d.	n.d.
Total Hexa-CDFs	40	60	-"-	-"-
Total Hepta-CDFs	8	8	-"-	-"-
Octa-CDF	5	5	-"-	-"-

n.d. = not detected

* = different isomers than those found in samples a and b

Table 31. PCBs RESIDUE FROM A TRANSFORMER VAULT FIRE, COLLECTED 4/16/82 IN MIAMI, FLORIDA (12).

Sample Location/Description	Type Sample	PCBs * (mcg/100 cm^2)
Inside Transformer Vault:		
wall behind removed transformer (soot)	swipe	434 **
top of primary cable above fire (soot)	swipe	389
primary cable support bracket (soot)	swipe	704
floor near base of isolating switch (dirt)	swipe	27400
ceiling near fire location (soot)	swipe	860
secondary bus near vault ceiling (dirt)	swipe	195
wall next to exit ladder (dust)	smear tab	2
rung of exit ladder (dust)	smear tab	79
Above Transformer Vault:		
sidewalk grating	smear tab	2
standing water at curb near vault	swipe	3
Fire Personnels′ Clothing and Equipment:		
sleeves of turnout coat	smear tab	< 0.1
top of boot	smear tab	< 0.1
inside helmet	smear tab	< 0.1
front of turnout coat	smear tab	< 0.1
inside helmet face shield	smear tab	< 0.1
outside facepiece	smear tab	< 0.2
smoke ejector fan	smear tab	> 31

* As Aroclor 1260 (used as standard for quantitation of samples).

** As mixture of Aroclor 1254 (231 mcg) and Aroclor 1260 (203 mcg).

Table 31 represents the results of the surface sample analyses for PCBs contamination. Samples taken within the vault showed the heaviest contamination. Turnout coats and other personal protective equipment were not found to be contaminated (probably due to the decision to allow the fire to self-extinguish). The only contaminated equipment at the station was found to be the smoke ejector fan. Results showed PCBs contamination of > 31 mcg/100 cm^2. Previous NIOSH investigations indicate normal background levels for PCBs on non-contaminated surfaces should be less than 0.5 mcg/100 cm^2.

Table 32 presents the results of the analyses of 6 bulk samples of soot and other fire residues for the presence of isomers of PCDDs and PCDFs. No PCDDs were detected in these samples, but PCDFs from trichloro- to hexachloro- isomers were detected in samples B1 to B6. The samples also exhibited high levels of PCBs through Cl_{10} and polychlorinated diphenylethers (PCDEs) through Cl_8. The highly toxic 2,3,7,8-tetrachloro- isomer was not detected in any of these samples.

Gas chromatograph/mass spectrometer (GC/MS) analyses of soot samples collected from the vault ceiling directly above the fire scene was also performed. Peaks identified included penta-, hexa-, and heptachlorobiphenyls and numerous alkanes mostly larger than C_{20} (12).

St. Paul, Minnesota

On June 22, 1982, a PCBs fire occurred at the Hill-Murray High School in St. Paul, Minnesota (13). NIOSH samples of surface wipes and air were obtained on June 23, 1982, and results can be seen in Table 33. Samples were again obtained on July 7, and results are presented in Table 34.

San Francisco, California

On the morning of Sunday, May 15, an electrical fire of unknown origin occurred in an underground transformer vault located at One Market Plaza in San Francisco adjacent to a 28 story high-rise. The vault, located beneath a

Table 32. RESULTS OF ANALYSES FOR PCDDs AND PCDFs IN BULK SAMPLES OF RESIDUE FROM MIAMI TRANSFORMER FIRE (12).

Isomers	Number Possible	Number Detected						Concentration In Sample (ng/g or ppb)					
Samples:		B1	B2	B3	B4	B5	B6	B1	B2	B3	B4	B5	B6
Mono CDD	2	0	0	0	0	0	0	ND	ND	ND	ND	ND	ND
Di CDD	10	0	0	0	0	0	0	ND	ND	ND	ND	ND	ND
Tri CDD	14	0	0	0	0	0	0	ND	ND	ND	ND	ND	ND
Tetra CDD	22	0	0	0	0	0	0	ND	ND	ND	ND	ND	ND
Penta CDD	14	0	0	0	0	0	0	ND	ND	ND	ND	ND	ND
Hexa CDD	10	0	0	0	0	0	0	ND	ND	ND	ND	ND	ND
Hepta CDD	2	0	0	0	0	0	0	ND	ND	ND	ND	ND	ND
Octa CDD	1	0	0	0	0	0	0	ND	ND	ND	ND	ND	ND
2,3,7,8-TCDD	1	0	0	0	0	0	0	ND	ND	ND	ND	ND	ND
Mono CDF	4	0	0	0	0	0	0	ND	ND	ND	ND	ND	ND
Di CDF	16	0	0	0	0	0	0	ND	ND	ND	ND	ND	ND
Tri CDF	28	6	0	0	0	0	6	180	ND	ND	ND	ND	110
Tetra CDF	38	6	0	0	0	0	7	530	ND	ND	ND	ND	280
Penta CDF	28	7	0	0	0	0	5	1000	ND	ND	ND	ND	290
Hexa CDF	16	3	0	0	0	0	4	180	ND	ND	ND	ND	100
Hepta CDF	4	0	0	0	0	0	0	ND	ND	ND	ND	ND	ND
Octa CDF	1	0	0	0	0	0	0	ND	ND	ND	ND	ND	ND
2,3,7,8-TCDF	1	0	0	0	0	0	0	ND	ND	ND	ND	ND	ND

Detection Limit = For PCDDs: 10 ng/g for samples B1, B5, and B6; 100 ng/g for sample B2, B3, and B4.
Detection Limit = For PCDFs: 10 ng/g for samples B1, B2, B5, and B6; 50 ng/g for sample B4; 100 ng/g for sample B3.
Sample Descripton/Location:

B1	Soot, dust, and dirt from top of primary cable support bracket, circuit #2.
B2	Residue from floor under isolating switch near burned transformer.
B3	Scrapings from ceiling above transformer.
B4	Scrapings from secondary bus.
B5	Vault wall near exit ladder.
B6	Scrapings of soot and dirt from smoke ejector fan used to exhaust smoke from vault during fire.

ND = Not Detected

Table 33. ANALYSES OF PCBs (REPORTED AS AROCLOR 1260) IN WIPE SAMPLES FROM THE HILL-MURRAY SCHOOL (13).

Sample Location	PCBs (mcg/100 cm^2) on 6/23/82	PCBs (mcg/100 cm^2) on 7/7/82
Vault room	100-5000	2-120
Vault door	< 5	
Corridor outside vault room	< 5	
Room 048	20	3
Boiler Room	< 5	
Cafeteria	0.22-0.24	< 0.05
Corridor leading to fieldhouse	< 0.05	< 0.05
Corridor wall across from room 109	0.26	< 0.05
Corridor wall adjacent to music suite	0.27	
Corridor wall leading to office	1.6	< 0.05
Outside room 106	5.8	
Room 106	0.61-0.95	0.8
Room 138	1.4-2.1	0.2-0.5
Gymnasium	0.29	
Athletic building lobby	0.14	
Priory	< 0.05	

Table 34. AREA CONCENTRATIONS OF PCBs (REPORTED AS AROCLOR 1260) AND CHLORINATED BENZENES (13).

			Airborne Concentration (mg/m^3)		
Sample Vicinity by Date	Sample Duration (Hours)	Sample Volume (Liters)	PCBs*	Total Trichloro-Benzene**	Total Tetrachloro-Benzene***
June 23, 1982					
Transformer Vault	2.54	137	0.05	22.6	18.2
Transformer Vault	2.52	136	0.09	17.6	25.7
Vault Doors	2.37	123	0.02	10.2	11.7
Room 018	3.06	165	0.004	0.73	1.21
Outside Room 109	2.67	144	< 0.001	0.12	0.26
Cafeteria	2.98	161	< 0.001	0.35	0.27
July 7, 1982					
Transformer Vault	2.82	169	0.007	0.331	0.651
Vault Doors	2.83	170	< 0.001	0.048	0.229
Outside Room 018	2.82	169	< 0.001	0.020	0.089
Outside Room 109	2.92	175	< 0.001	0.011	0.037
Cafeteria	2.92	175	< 0.001	0.010	0.032

* NIOSH recommended permissible exposure limit for an 8-hour time-weighted average (TWA) exposure criteria is 0.001 mg/m^3.

** ACGIH threshold limit value is 40 mg/m^3 for 8-hour TWA. Neither NIOSH nor OSHA have exposure criteria.

*** No 8-hour TWA exposure criteria.

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sidewalk manhole grate, contained three Pacific Gas and Electric Company (PG&E) owned transformers and associated network protection equipment. Each of the three transformers was filled with approximately 515 gallons of PCB fluid.

During the course of the fire, a cooling fin on one of the transformers was damaged, resulting in the release of approximately 50 gallons of PCB fluid. The fire burned and smoldered for approximately eight hours after discovery. Subsequent sampling of the building and surrounding area indicated that PCBs and by-products of PCB combustion had been released through the sidewalk grate, through conduits into the buildings switchgear room, and through discontinuities in the vault wall into an adjacent basement garage. The ventilation system serving floors B-2 through 6, which draws air from a point near the switchgear room, was also shown to have surface contamination of PCBs and combustion by-products.

Samples taken and analyzed after the incident revealed that the transformer oil involved was 100 percent Aroclor 1242. The dielectric fluid itself contaminated the vault, while smoke from the vault contaminated the vault, portions of basement B-1 and basement B-2, the exterior wall of the Steuart Street tower near the vault, the brick sidewalk near the vault, and portions of the air handling system that supplies floors B2 through 6.

Sampling for PCBs and TCDFs in the vault after the fire, prior to clean-up, revealed the following (highest recorded) contamination levels:

Sample	PCBs	TCDFs
Soot from manhole cover	110,000 ppm	--
Wipe sample from floor	910,000 mcg/100 cm^2	--
Soot from vault wall	--	15.6 ppm

Extensive air sampling was conducted during the clean-up operations. Approximately 4000 air samples were taken in various locations inside and outside the high-rise tower to monitor decontamination efforts. The highest air concentrations were measured in the vault; the second highest concentrations were found in the switchgear room, adjacent to the vault. Prior to cleaning, air samples in the vault revealed PCBs levels up to 1,500 mcg/m^3 and air samples from the switchgear room showed PCBs levels up to 98.6 mcg/m^3. The highest level outside the vault and switchgear room was found in a storage room, where a level of 12 mcg/m^3 was measured.

Other Fires

There have been a host of other fires associated with PCB transformers and capacitors. Many in the U.S. probably go unreported. The following are some of the fires reported in the Scandinavian countries:

Location	Category	Date
Aruika (Sweden)	Explosion in PCB filled capacitor	May 1982
Imatra (Finland)	Explosion in PCB filled capacitor	Aug 2, 1982
Helsinki (Finland)	Explosion in PCB filled capacitor	Aug 1982
Surahammar (Sweden)	PCB fires with mineral oil as the external energy source	Sept 23, 1982
Hallstahammar (Sweden)	Explosion in PCB filled capacitor	Nov 8, 1982
Railway locomotive (Sweden)	Explosion in PCB filled capacitor	Winter 1982/83
Kisa (Sweden)	Explosion in PCB filled capacitor	Apr 25, 1983
Halmstad (Sweden)	Explosion in PCB filled capacitor	Aug 15, 1983

In September 1982, a 500-unit capacitor battery at a steel mill in Surahammar, Sweden, was ignited by 10 tons (9090 kg) of molten steel. The capacitors were filled with PCBs [2 tons (1820 kg)] and mineral oil [3 tons (2730 kg)]. The fire burned for 2 to 3 hours, and filled the entire building with smoke. Table 35 presents the results of analyses of wipe samples.

Table 35. PCDFs FOUND AT SURAHAMMAR, SWEDEN (ng/m^2)*.

Sample Location	TCDFs	2,3,7,8-TCDF	Cl_5	Cl_6	Cl_7	Cl_8
Capacitor Room (Sample 1)	4000	875	3300	1800	1500	300
Capacitor Room (Sample 2)	1100	365	1250	940	625	145
N.E. Corner, 10 m height	1250	300	355	150	65	13
S.E. Corner, 10 m height	480	120	210	140	60	30
N.E. Corner, floor	100	25	27	15	5	2
S.E. Corner, floor	90	22	25	17	17	4
10 m Outside, downwind	<250	<25	<25	<60	58**	17**
300 m Outside, downwind	<250	<25	<25	<60	<30	<12
After Cleaning (Sample 1)	<20	<4	<10	<12	<15	2**
After Cleaning (Sample 2)	<40	<8	<20	<20	<30	6**

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* Wipe tests.

** Possibly due to Cl_9 or Cl_{10} PCBs in casting sand.

There have been several other capacitor fires after which PCDFs were found, such as those at a paper mill in Imatra, Finland (August 1982), and Volvo in Skovde, Sweden. Table 36 presents a comparison of the gross PCDF levels from several incidents.

Table 36. PCDF LEVELS IN PCBs FIRES.

Site	PCDF Levels	PCBP Levels*
Skovde (foundry, well-ventilated)	0.01 mcg/m^2	None
Skovde (basement capacitor room)	0.8 mcg/m^2	None
Danniken, Sweden	1.5 mcg/m^2	1.5 mcg/m^2
Surahammar, Sweden	1-10 mcg/m^2	Less than PCDFs
Imatra, Finland	1-3 mcg/m^2	Less than PCDFs
Imatra, Finland	1.5 ppm	
Binghamton, New York	2160 ppm	Less than PCDFs

* Quantification not possible due to the lack of standards.

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SECTION 6

PREVENTION AND MANAGEMENT OF PCBs FIRES

Fires and catastrophic failures involving PCBs transformers, capacitors and other PCBs-containing electrical equipment have occurred in many countries in a variety of buildings and facilities. Such incidents will undoubtedly recur. This section essentially presents the current thinking of people within government, the electrical utilities, fire fighters and academics who have been involved with PCBs transformer and capacitor fires. The lack of carefully evaluated scientific data and empirical evidence does not lessen the validity of the thinking, suggestions and approaches discussed in this section. PCBs fires do not represent carefully conducted scientific experiments.

EARLY PREVENTIVE MEASURES

Phase-out of PCBs-Containing Electrical Equipment

The removal of all PCB-containing electrical equipment may appear to be the ideal solution, but there are a number of practical considerations which currently limit this approach. First, there is the question of the cost. Because PCBs electrical equipment still forms a major core of the electrical equipment still in service, there would be substantial cost to the utilities, building owners and ultimately the consumers if all the equipment is replaced immediately. The second consideration deals with available substitutes. PCBs usage as the dominant heat exchange fluid for transformers and capacitors over the years is due to the fire safety properties offered by PCBs low flammability. Eliminating PCBs at this time would mean a reversal to the use of mineral oil which is substantially more flammable. A number of new heat exchange fluids are now offered as PCBs substitutes. In addition to the higher cost, very little is known about the toxicities of these new materials and their use could create an even higher risk to the environment. Finally, there is also the problem of responsibility and liability. Ownership of PCBs-containing electrical equipment is mixed. In some instances, the equipment is owned by the utilities and in others it is the property of the building owners.

Following the PCBs transformer fire at One Market Plaza in San Francisco, Pacific Gas and Electric (PG&E) has adopted a policy of gradual phase-out of its PCBs transformers and capacitors. Under a consent decree with the city government, PG&E agreed to phase-out over a two-year period, more than 400 PCBs-containing transformers. These 400 transformers were selected on the basis of their location in high population density areas such as office buildings and metro stations. Similarly, Florida Power and Light Company (FPLC) has announced plans to replace 458 PCB-transformers over a five-year period.

Better Information Exchange and Coordination with the Local Fire Fighting Departments

Electrical utilities can assist local fire fighting departments with better information on the problems associated with PCBs fires. Fire departments should know the number and location of PCBs transformers and capacitors within their jurisdictions. In the May, 1983, PCBs transformer incident at One Market Plaza in San Francisco, the fire fighters who initially responded to the fire were not aware that a PCBs transformer was involved. Filmed accounts of the fire indicate that when a tremendous amount of black smoke poured out of the underground sidewalk vault housing the PCBs transformers, no respiratory protection was used by the fire fighters present above the transformer vault during their response to the fire. PG&E now provides the San Francisco fire department and other fire jurisdictions, listings of the locations of PCBs transformers and capacitors.

Improvements in Labeling of PCBs Electrical Equipment

All PCB-containing electrical equipment is now required to be labeled under EPA regulation. However, this labeling may not be readily visible or apparent in the case of a fire. Highly visible labels or signs should also be placed in other areas near the transformer to indicate that a PCBs-containing transformer(s) is in the building. Examples of areas include primary entrance points to the building likely to be used by emergency response personnel and outside the vault on the door. These labels should be on the transformer vault doors at heights of 2- and 5-feet above the floor. The label at the 2-foot height would likely be visible to a fire fighter crawling in a smoke filled room.

De-energizing and Power Disconnect

Electrical utilities, owners and/or operators of the equipment should retrofit the equipment to assure that electrical power could be rapidly disconnected in the event the transformer enters a failure mode. The primary load breaker air switch on the high-voltage side of the transformer should be located outside of the equipment vault. This would allow a rapid disconnect of the electrical power and also remove the need to enter the vault containing high concentrations of PCBs and associated pyrolysis products. The gang operated fused air switch on the utility pole should be considered as the secondary procedure because it requires a service person from the utility company to disconnect the power. Such a person may not be available immediately.

RESPONDING TO PCBs-CONTAINING ELECTRICAL EQUIPMENT FIRE EMERGENCIES

Fire fighting has long been recognized as a dangerous profession. Over the years, many successful steps have been taken to reduce the intensive hazards and to increase the safety of fire fighting personnel. Better training and advances in protective equipment have substantially improved safety for fire fighting personnel. Yet, none of the existing protective measures completely eliminate exposure to very low level concentrations of highly toxic materials, such as PCBs and their pyrolysis products.

When fire emergencies involving PCBs occur, the responding fire officers must make some very difficult decisions. The fire officers′ decisions can be facilitated the more informed they are with regard to the size and location of the equipment. No specific protocols for fighting PCBs fires have been developed by the fire fighting departments or the electric utilities.

Response operations during the initial phase of a fire incident involving PCBs-containing transformers or capacitors requires familiarity with response organization and management, the uses and limits of equipment and apparatus, site entry, control, and decontamination procedures. Fire officers in command of such fire emergencies should examine all issues and make decisions using the three-step process of recognition, evaluation, and control.

Recognition

Recognition consists of determining the hazard and its degree of risk. When an emergency involves a fire, a fire officer′s first decision is whether it is safe to attempt to fight it. Sometimes the best approach may be to let the fire burn, especially if it is in an isolated storage area. If fire fighters are likely to be exposed to PCBs in the emergency situation, the following elements should be recognized and considered:

1. What is the situation?

What is involved? Is it a transformer? At what location or within what area? What is the maximum potential danger? Is life safety threatened; if so, to what extent? What other damage can occur?

2. What are the hazards?

What is the PCBs concentration in the transformer or capacitor? What is the capacity of the electrical equipment? What is the total amount of PCBs involved?

3. What are the safety measures?

How much area will be needed for control operations? How much time is available? Is it necessary to evacuate nonemergency personnel from the dangerous zone? What extent of evacuation is necessary? What protection will be needed for fire fighters and others working at the scene? What are the influences of wind, terrain, water supply, vehicular traffic, and thoroughfares?

4. What are the capabilities available?

How many emergency personnel are available and are they trained for the situation? Are reserve forces ready for immediate response? What apparatus, equipment, and extinguishing agents are available? How close to the scene can you operate? What are the best locations for placing and moving apparatus and personnel?

Evaluation

Evaluation provides judgment based on the information obtained in the recognition phase and gives response personnel an understanding of the hazards.

Once a decision is made to fight the fire in the presence of PCBs-containing electrical equipment, the following precautions should be observed:

- Approach the fire from upwind, wearing self-contained breathing apparatus.
- Evacuate occupants of building which may be downwind of toxic gases and smoke.
- Be careful to avoid touching PCBs with bare hands. Keep hands which may have contacted PCBs away from eyes and mouth.

- Keep cooling streams of water on drums as well as on cylinders that are exposed to heat, so as to prevent flame impingement, fusing of the safety devices, or rupture of the cylinders which have no safety devices.

- Use water spray streams to flush pathways, disperse vapors, and to protect men attempting to shut off a valve to stop the flow, or who are trying to plug a leak.

- Foam can also be used. A more detailed description will be discussed later.

- Wear full protective clothing (in addition to respiratory protection), including boots and gloves, during fire fighting and overhauling operations.

The fire fighter may attempt to stop leakage in the PCBs-containing electrical equipment which is not on fire by closing valves or plugging holes. However, full protective clothing is required for handling PCBs. Fire fighters must also be careful not to splash PCBs on themselves. Another alternative is to transfer the contents of or to relocate a drum or tank car away from an exposed area to a safer location before trying to stop the leak.

Control

The control step addresses all potentially feasible controls. It is based upon the information obtained from the previous steps of recognition and evaluation, and is used to determine the most feasible mitigation process. In order to control and handle PCBs fire situations, adequate protective clothing, equipment and fire extinguishing chemicals are necessary to ensure personnel safety.

Protection of Fire Fighters and Other Emergency Response Workers

The highest priority in responding to a PCBs transformer incident is to prevent exposures to the emergency response workers such as fire fighters and paramedics. Early prevention measures discussed previously can substantially prevent fire fighters' exposures. First, correct labeling of PCBs-containing transformers will allow early recognition of the hazard in the event of a fire. Second, the location of primary load breakers should be known to permit rapid power disconnect by authorized personnel. In any case, the number of fire fighters exposed to the smoke from the burning transformer should be limited. The smoke from such a fire must be considered extremely hazardous as it may contain PCBs and their highly toxic pyrolysis products PCDFs and PCDDs.

In general, three levels of protective equipment are needed. Table 37 contains the different levels of equipment that are currently available and utilized in hazardous chemical emergencies response.

The first category, Level 1, is the maximum level of protection provided to the personnel for the normal operations. Level 1 protective equipment is designed to be worn by workers and technicians when working on the spill site when there is a reasonable potential for direct contact with the PCBs material. Level 2 safety equipment is worn by all other on-site personnel. In a PCBs fire situation, Level 3 protective equipment should be used.

To ensure the adequacy of the protective equipment, a personnel and environmental monitoring program should be developed. Air samples should be continuously collected from the breathing zone of all workers to check for contaminated particulate matter such as PCDDs and PCDFs. All personnel involved in PCB fire fighting should also be required to participate in some follow-up health and safety program which includes medical monitoring and safety training.

Fire fighters who are expected to be exposed to the smoke should wear a self-contained breathing apparatus (SCBA) operated in the positive pressure mode and standard turn-out gear (Level 2). Although the neoprene vapor barrier commonly used in fire fighter protective clothing may not prevent penetration by vaporous PCBs and other compounds, practical alternatives are not readily available. When possible, flame resistant disposable protective clothing should be worn over the usual primary protective turn-out gear. This use of disposable protective clothing will serve as a barrier against combustion particulates and ultimately reduce the problem of decontamination

Table 37. PERSONNEL PROTECTIVE EQUIPMENT

Level	Equipment
1	Cap with air-line respirator PVC chemical suit Chemical gloves taped to suit, leather gloves as needed Work boots with neoprene overshoes taped to chemical suit Cotton overalls/underclothing/socks (washed daily) Cotton glove liners Walkie-talkies for communication Safety glasses or face shield
2	Positive pressure self-contained breathing apparatus PVC chemical suit Chemical gloves, leather gloves as needed Neoprene safety boots Cotton overalls/underclothing/socks (washed daily) Walkie-talkies for communication Safety glasses or face shield
3	Hard hat Air purifying respirator with chemical cartridges PVC chemical suit and chemical gloves Work boots with neoprene overshoes taped to chemical suit Cotton overalls/underclothing/socks (washed daily) Cotton glove liners Walkie-talkies for communication Safety glasses or face shield

of the turn-out gear. Similarly, all fire equipment such as air ejection fans, hoses, non-disposable protective equipment, etc., exposed to the smoke should be properly decontaminated using an alkaline or nonionic synthetic detergent. To assure that all materials have been adequately decontaminated may require laboratory analysis or the disposal of the materials.

Fighting PCBs Fires

One of the greatest needs at this time is the development of a generally accepted protocol for fighting and putting out fires involving PCBs electrical equipment. Neither the fire fighters nor the electric utilities have reached any consensus on what are the best ways to respond to a PCBs transformer/capacitor fire situation. There are substantial differences as evidenced in recent negotiations between the fire fighting union of a major West Coast city and the electric utility. The electric utility believes that the PCBs fires should be treated like any other fire and fought with water after power disconnect and de-energizing. The fire fighter union believes that PCBs fires are unique and in many instances no attempt should be made to fight it and the fires should be allowed to burn out with the aide of incendiary halides. The unions also wanted the electric utility to provide special CO_2 cylinders and training to the fire fighter to combat PCBs fires.

Technical weaknesses can be identified on both sides on the issue. PCBs transformers/capacitors fires are not similar to any other fire because of the toxic residues that they generate and their long lasting contamination. Every effort should be made to put out the fire as quickly as possible in order to minimize the amount of highly toxic pyrolysis products that are generated. Allowing a fire to burn itself out may result in the in-situ thermal production and dispersion of a large number of highly toxic PCDFs, PCDDs, PCBPs, PCPYs, PCCYs, PCNs, etc.

In addition to water, special chemical agents have been utilized to fight fires involving hazardous chemicals. The most common agents are chemical foams. These foams can be divided into the following categories:

- Protein Foam
- Aqueous Film Forming Foams
- Fluoroprotein Foam
- Synthetic Foam
- Chemical Foam.

Protein-based foam is formed from the decomposition of vegetable or animal proteins, with metallic salts added for strength. There are two basic concentrations, 6% and 3% in water (i.e., 94% and 97% water is added). Air is added to the mixture to expand the solution into the finished foam product.

The expansion ratio of protein foams varies between the manufacturers from 1:7 to 1:12. Foams with this type of air ratio are known as low-expansion foams.

Aqueous film forming foam (AFFF) uses several chemicals called fluorocarbon surfactants to function. These groups of chemicals operate by altering the physical properties of water (reducing the surface tension) so that they are able to spread and float across the surface of a hydrocarbon fuel even though they are more dense. Because of this property the foam has been called "light water." Like protein foam, AFFF is available in 3% and 6% concentrations.

A further refinement of AFFF is the combining of the fluorocarbon surface active agents with protein foam. This combination is called fluoroprotein foam. Variable physical properties can be achieved by varying the proportions of the two products.

The low expansion foams, protein, AFFF, and fluoroprotein extinguish fires involving flammable liquids by:

1. Excluding air from the flammable vapors.

2. Eliminating vapor release from the fuel surface.

3. Separating the flames from the fuel surface.

Another class of fire fighting foams is the synthetic detergent type. These are sometimes referred to as high expansion foams because of their expansion ratios in the order of 1:15 and 1:20. They use ordinary, air-aspirating equipment.

These foams flow well, are capable of rapid flame breakdown, and can gain control of hydrocarbon fires at low to moderate solution application densities. Ultra-high-expansion foam is produced in specialized equipment by driving a high-volume air stream, by means of a fan, through a metal or cloth grid which is continuously sprayed with a synthetic foam solution at a predetermined rate and concentration. Expansion ratios of 1:800 have been achieved, depending upon the type and chemical composition of the foam as well as its stabilizers.

Chemical foam is formed by the reaction of an alkaline material with an acid in the presence of a stabilizer. The two products to mix come in either powder form or a liquid solution. The acid solution is aluminum sulfate and the alkaloid material is sodium bicarbonate. This foam is infrequently used due to the inconvenience of mixing plus the time delay required for application. In addition, getting the foam on the fire requires special application tools, which adds another delay factor.

ASSESSMENT

After the fire, access to areas possibly contaminated by the fire must be limited until the extent of contamination can be determined. This is important to prevent further exposure to humans and to avoid transferring contaminants to clean areas. Next step is to determine the extent and relative degrees of contamination of the area. The intent is to develop quantitative information as input for the decisions in defining the nature and extent of the decontamination and clean-up effort. Areas of contamination can be identified and boundaries of the areas defined by visual observation and analytical determinations. While combustion soot characterized as a black, friable carbonaceous material may be visible on surfaces contaminated by a transformer fire, the full extent of contamination will not be known until extensive wipe sampling has been completed. This initial wipe sampling should focus on PCBs spread by the fire. PCBs-contaminated areas can best be identified by collecting sufficient wipe samples to delineate the extent of both vertical and horizontal contamination in terms of mass per unit area of surface such as mcg/100 cm^2 or mcg/m^2. Sufficient wipe samples also must be obtained to determine background levels for an area unaffected by the incident. These samples are necessary to derive the relative degree of contamination by comparing the sample analyses from the contaminated areas to the background level values.

While PCBs surface wipe samples are useful in establishing the extent and degree of contamination, sampling for PCDFs and PCDDs is necessary to establish an unequivocal assessment of the contamination. Bulk soot samples obtained by vacuuming a unit area of surface are preferred for this analysis, but wipe samples as described above may also be used. The sample should be initially submitted for a PCDF and PCDD isomer-group (mono- through octachloro compounds) analysis. If this analysis shows that the tetra- or pentachloro isomer-groups are represented, then an isomer specific analysis should be conducted for 2,3,7,8-TCDD, 1,2,3,7,8-PCDD, 1,2,3,7,8,9-HCDD, 2,3,7,8-TCDF and 1,2,3,7,8-PCDF. The collection of air samples for PCBs and PCDFs or PCDDs may be necessary to define the level of personnel protective equipment used by clean-up workers.

REOCCUPANCY CRITERIA

There are no Federal guidelines to define acceptable clean-up levels for toxic releases from PCB transformer fires. TSCA regulations do state, however, that all spills and leaks of PCBs should be cleaned up to pre-existing background levels whenever there is a threat of contamination of water, food, feed or human beings. NIOSH has found background levels in urban areas up to 0.5 mcg PCBs per 100 cm^2 of surface area. In the absence of certain PCDF and PCDD isomers, the mitigation effort could be directed at clean-up of the PCBs contamination to 0.5 mcg per 100 cm^2 of affected area. In terms of airborne exposure, the NIOSH recommended guideline for the workplace is 1.0 mcg PCBs per cubic meter of air.

The State of New York has proposed the following guidelines for reentry (3):

- Average Daily Intake (ADI) = 2 pg/kg/d for 2,3,7,8-TCDD
- Air
  - Inhalation Exposure = 10 pg/m^3 of 2,3,7,8-TCDD
    = 39 pg/m^3 of 2,3,7,8-TCDF
- Surface
  - Ingestion from Dermal Exposure = 3 ng/m^2 (minimum) - 28 ng/m^2 (maximum) of 2,3,7,8-TCDD
    = 12 ng/m^2 (minimum) - 110 ng/m^2 (maximum) of 2,3,7,8-TCDF

In response to the One Market Plaza fire incident clean-up, the San Francisco Health Department and the California State Department of Health Services issued the following guidelines for safe reentry levels:

a) for decontaminated areas (4):

- Air Exposure = 10 pg/m^3 of 2,3,7,8-PCDD/PCDF*
  = 1.0 mcg/m^3 of PCBs

- Surface Exposure = 3 ng/m^2 of 2,3,7,8-PCDDs/PCDFs*
  = 100 mcg/m^2 of PCBs

b) for the area inside the PG&E vault:

- Air exposure = 80 pg/m^3 of 2,3,7,8-PCDDs/PCDFs
  = 1 mcg/m^3 of PCBs

- Surface exposure = 24 ng/m^2 of 2,3,7,8-PCDDs/PCDFs
  = 1 mg/m^2 of PCBs

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* Above background levels. All PCDD and PCDF levels excluding octa-CDDs/CDFs.

Reoccupancy criteria have also been evaluated in Sweden and Finland. In Sweden, the accepted surface guideline value was 50 ng/m^2 of 2,3,7,8-TCDF. Finland's reoccupancy criteria are still being discussed, but the suggested surface guidelines are (5):

- 5 ng/m^2 of 2,3,7,8-TCDF
- 50 ng/m^2 of total TCDF
- 5 ng/m^2 of 2,3,7,8-TCDD.

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SECTION 7

DECONTAMINATION OF BUILDING AND FINAL DISPOSAL OF PCBs-CONTAMINATED MATERIAL

BUILDING DECONTAMINATION

General Consideration

When a building is being decontaminated following an accident involving toxic material such as PCBs, precaution must be taken before work commences to ensure that the presence of a toxic chemical will not cause problems. The decontamination must be carefully planned if it is to be safely carried out. In comparing options for decontaminating and possibly dismantling a building and its interior, it is important to consider all the possible routes of exposure to the toxic chemical. These include:

- handling contaminated fixtures, materials and contents of the building
- handling contaminated material during dismantling and decontamination
- transfer of contaminated material
- preparing the materials for transport
- transport of material
- handling materials at the disposal site
- final disposal

Three overall strategies are usually considered for the "clean-up" of a contaminated building (1). These are:

- construction of a monolith
- comprehensive decontamination of the building, followed by dismantling and disposal of the contaminated wastes removed from the building
- containment of the contaminated solid materials as far as possible, within the site

Construction of a Monolith

The first option which needs to be considered is to leave the contaminated material in its present location, by turning the building into a concrete monolith. Constructing such a monolith involves:

- clean up loose debris and dismantle old fixtures and furniture and place in containers
- coat all surfaces with polymeric coating material to prevent migration of contamination during working
- coat the highly contaminated transformer/capacitor and other equipment with a thick layer of resinous material in order to provide an additional protection against subsequent release
- reinforce outside walls of the building, or that part of the building which it is planned to retain
- fill the building with concrete, taking care to fill all spaces between pipes, etc.
- if desired, demolish those parts of the building which are both not contaminated and not essential to the integrity of the monolith
- seal the monolith to prevent, as far as possible, the ingress of water
- landscape the monolith.

The principal advantage of this approach is that it reduces contact of the workers with the contaminated area, once the loose debris has been cleared and the surfaces coated. The disadvantages are many. It is impossible to guarantee that the monolith will remain intact indefinitely. The effects of weathering and/or flooding might lead to fissuring of the concrete and water ingress, with a chance of leaching out. Socially, the monolith will be aesthetically unattractive, and will serve as an unwelcome reminder of the accident.

Comprehensive Decontamination

Comprehensive decontamination of the building would have as its objective the restoration of the building to its original use condition. Various techniques are available for the decontamination of external surfaces, but they are either difficult to apply to complex surfaces (e.g., mechanical methods, vacuuming), or they offer a high risk of contaminating the workers or the environment (e.g., solvent or steam cleaning).

Decontamination of the interior of the building and its ducts, wirings and plumbing poses even greater problems. Some of the ducts contain tarry deposits which could be difficult to remove. Even if the contents could be safely removed, the internal surfaces would still have to be decontaminated. The success of such an operation could not be adequately monitored, as it would be impossible to check all internal surfaces for freedom from PCBs, PCDFs and PCDDs. Thus, even if comprehensive decontamination could be achieved, it would still be necessary to dispose of the equipment as if it contained some residual contamination. Any decision to decontaminate maximizes exposure of the workers to the highest levels of contamination and generates larger quantities of highly contaminated liquid wastes for disposal.

Direct Disposal

The third option is that of "direct disposal". In this, no specific attempt is made to remove contaminated material from the ducts and pipework. The building is dismantled as directly as possible, the majority of the contaminated materials being sealed into the original ducts and pipes: obviously any liquids or loose solids encountered during dismantling are removed and disposed of separately.

Comparing direct disposal with the previous option of comprehensive decontamination, the main advantage is that handling of the most highly contaminated materials is minimized. The problems of dismantling are largely common to both options. Transport and direct disposal yields mainly equipment with contaminants sealed inside, while decontamination yields both nominally clean equipment and highly contaminated, mainly liquid, wastes.

Operations in PCBs transformer vaults have the potential to spread contamination and put the work force at risk. The control techniques are very similar to those used for dismantling plants contaminated with radioactivity, asbestos, mercury, etc. All these operations at some time involve taking contaminated items from a highly contaminated zone into a clean zone in a safe manner.

Combustion soot from a transformer fire is a black, friable carbonaceous material that does not adhere strongly to surfaces unless it has been ground in by pressure. Initial clean-up of the soot should be achieved by dry vacuuming of both horizontal and vertical surfaces. Subsequently, the degree of residual contamination should be determined by how much additional cleaning needs to be done to comply with the established reoccupancy criteria. During the initial clean-up phase, control zones and procedures should be established and implemented to prevent redistribution of the soot to other areas. For instance, if the transformer incident involves a multilevel building, high efficiency particulate filters should be installed in the air circulation system to prevent movement of soot from one floor to another through the ventilation ducts.

Nonionic and alkaline synthetic detergents have been used to effectively decontaminate most surfaces. The synthetic detergents have the advantages of not having a flash or fire point, and can be applied manually through power scrubbers, power sprayers and steam cleaners. In addition, the detergent and rinse (normally water) solutions are easily picked up by wet vacuum cleaners and treated to remove all toxic materials before being released to the sanitary sewers.

Ultimate clean-up methods may involve washing surfaces with organic solvents highly compatible with PCBs such as deodorized kerosene, methylene chloride, or a mixture of 1,1,1-trichloroethane and trichlorobenzenes. Although these solvents may effectively decontaminate certain porous and nonporous surfaces, they are not routinely used for two reasons. First, the problems associated with removal and disposal of the spent decontaminant material. Second, the generation of potentially high concentrations of an organic vapor that will reduce the service life of the carbon cartridge respirators used by clean-up workers.

The use of an organic solvent may even be inadequate to reduce the level of surface contamination below the reoccupancy criteria. Concrete floors and walls in transformer vaults and switch gear rooms may occasionally be one such example. In these situations, an elastomeric, abrasion and flame resistant sealant should be applied to the surfaces. Consideration also should be given to applying such a secondary containment system to surfaces in vaults and PCBs-equipment rooms prior to a failure incident. A secondary containment system would facilitate both efficient recovery due to the decreased porosity of the surface and rapid clean-up.

Clean-up at the Binghamton State Office Building PCBs Transformer Fire Site

The Binghamton State Office Building forms a prominent central tower within a governmental building complex shared by the State of New York, the County of Broome, and the City of Binghamton. The State Office Building, completed in the spring of 1973, rises 18 stories (260 feet) above street level and has two sub-surface levels. Thirty-three State agencies normally occupy the State Office Building, with approximately 700 employees. The following provides an overview in a chronological manner, the major efforts undertaken and scheduled to resolve the problems resulting from the fire. Material was adopted from a progress report filed by the Office of General Services of the State of New York in January 1983.

On Thursday, February 5, 1981, the Office of General Services (OGS) in Albany, was notified that there had been an electrical fire and subsequent power failure at the Binghamton State Office Building. The fire occurred at approximately 5:30 a.m., and the building was unoccupied with the exception of a Security Guard and a Stationary Engineer.

Since the markings on the transformer indicated that the oil contained polychlorinated biphenyls (PCBs), the OGS engineering staff initiated necessary action in accordance with the applicable regulations of the federal Environmental Protection Agency (EPA) and the New York State Department of Environmental Conservation (DEC). New England Pollution Control (NEPCO) arrived mid-afternoon and, outfitted with protective suits and respirators, began to clean the floor of the transformer room.

Workers established a temporary electrical system, cleaning of the mechanical equipment room proceeded, and DEC was contacted as to the proper disposal of the hazardous materials. A complete inspection of the building revealed that a fine soot had been distributed throughout all areas of the upper floors. The estimated time required for clean-up was extended from several days to several weeks. It was also determined that the New York State Department of Health would arrange to more fully characterize the chemical contents of soot and air samples. Sampling began on Friday the 6th and continued on a near daily basis through February 27th.

Early Saturday morning, the County Health Commissioner received the test results. The air samples contained 6-62 mcg/m^3 of PCBs and the soot registered PCBs levels of from 10 to 20 percent. The County Health Commissioner concluded that the air was relatively clean in light of the fact that levels were below the allowable standards promulgated by the Occupational Safety and Health Administration (OSHA). The test results were relayed to OGS in Albany along with samples to be tested further by the State Health Department. Blood samples were taken. Personnel working within the building continued to wear respirators and air samples for testing were collected on a regular basis.

On Sunday, February 8th, New England Pollution Control began the clean-up of the overhead areas in the mechanical equipment room, so that the area could again be used to house the power distribution system. Test results indicated that the levels of PCBs contamination in the air samples were still well within OSHA standards.

Early during the week of the 9th, Department of Health staff inspected the building, and arranged for the collection of additional soot and air samples. The DOH team also presented OGS with a Safety Plan which was approved by the Occupational Safety and Health Act (29CFR) providing the basic safety program for the operation. The Plan addressed security, showers and change areas, safety equipment, respiratory protection, and sampling schemes. All surfaces contaminated by soot and smoke particles were to be cleaned initially by a high-efficiency vacuum and washed with water and detergent. Exposed surfaces not easily cleaned; such as papers, carpets, drapes, etc., were put in plastic bags and removed to a storage area in the sub-basement. Cleaned areas were sampled for PCBs by wipe testing. The State issued instructions to have all water discharged from the building during the cleaning deposited into 55-gallon barrels to await treatment and final disposal.

By mid-week, in accordance with the Safety Plan, the collection of blood samples from all personnel who were working in or had entered the building was initiated.

It was during this week also that the cleaning of the mechanical-equipment room was completed and necessary temporary electrical connections accomplished. The temporary power distribution system was ready for installation. Representatives from the Department of Environmental Conservation (DEC) also arrived to provide technical assistance.

By Friday, the Department of Health reported finding PCBs in all soot samples tested, indicating that the contamination was widespread in the building.

Based upon the findings of the Health Department tests, soot samples from the basement and parking areas were taken. DEC took water samples for testing from the nearby Susquehanna River and also supervised the preparation of the 55-gallon drums that were to be used for the shipment of debris.

The State decided, during the week of February 16th, that based on the test results from both the Department of Health and Galson Technical Services, the basement parking area would also be treated as a contaminated area. While waiting for the definitive results of the tests of the samples taken from the parking garage, precautionary measures were taken. Revisions to the Safety Plan were made so that personnel would no longer enter and exit at the parking garage level. By that week, CECOS International, Inc., a licensed waste disposal firm that had been hired by the State, had removed 230 barrels of toxic waste from the building for disposition in a secure and certified landfill.

Repeat medical examinations were performed on cleaning personnel and others who were determined to have been exposed to any contaminated material. Furthermore, DEC commenced sampling of ambient air to determine current PCB levels.

On Thursday, February 19th, National Institute of Occupational Safety and Health (NIOSH) representatives reviewed and approved the Health and Safety Plan and trained two OGS personnel to act as safety observers throughout the clean-up effort.

Since the duration of the clean-up effort was not able to be definitively determined, OGS began considering long-term alternative office space in which to continue business of government.

On February 20th, DOH released its first analytical report regarding samples taken from the buildings, and on the week-end of February 21st, Department of Health testing confirmed that PCBs contamination had been found in samples taken from the parking garage area. DOH recommended that the area be cleaned.

The next day, clean-up of the parking garage began. After consultation with DEC and New England Pollution Control, a treatment system for the water discharged from the building was constructed. Since large volumes of water would be generated by the cleaning procedures, a treatment plant was built in the sub-basement level of the parking garage. This treatment plant consisted, at the time, of two above ground swimming pools initially having a capacity of approximately 13,000 gallons each. The water was collected in one pool and pumped through two high rate sand filters to remove any large particulate matter which might exist. The water was then pumped into a column of activated carbon and allowed to run through, by gravity, into the second pool. This water was then tested and, when acceptable chemical levels were reached, was discharged into the sanitary sewer system of the city in accordance with the terms of the permit issued by the City of Binghamton. This system has now been expanded to 3 pools.

On Wednesday, February 25th, the State Health Department informed OGS that their (DOH) analysis indicated that in addition to the previously detected levels of PCBs, the soot also contained lesser amounts of dioxin and dibenzofuran. Upon being apprised of this information, it was determined that a request for proposal (RFP) to clean the building would be developed by the Office of General Services working in cooperation with the State Health Department, Labor Department, and the Department of Environmental Conservation, as well as appropriate Federal agencies and acknowledged experts.

Photodocumentation of the building's condition began and, at the request of OGS, the Department of Health began to assemble a panel of internationally renowned chemists and physicians, to meet in early April in New York City, to focus on medical issues related to the event.

DOH began taking samples of air on the building's 7th floor from March 12th through March 18th.

During the week of March 16th, DEC tests of samples of air taken from outside the building resulted in no measureable levels of PCBs. By that time, DOH had circulated information on toxicology protocol for approval by appropriate parties.

In that same week, the membership of the expert panel was finalized. Its members included physicians, chemists, toxicologists, epidemiologists, engineers, and representatives from various federal and state agencies, as well as Canada. The panel met at New York's Laguardia Airport on April 3rd. The results of the expert panel meeting were used as the basis for a request for proposal (RFP) from independent firms specializing in the development of plans and the supervision of the execution of such plans regarding toxic chemical decontamination projects.

On Wednesday, April 1, 1981, the Office of General Services hired Versar, Inc., a Virginia-based engineering and research firm, specializing in working with toxic and industrial chemicals, to advise and develop clean-up procedures, air pollution control plans, and primary clean-up plans.

Events during the first week in April included Versar's representative, as well as members of the expert panel, arriving to tour the building. Their recommendation was that further biological and chemical testing be done. At the State's request, the National Institute of Occupational Safety and Health agreed to act as lead agency in the implementation of the Medical Surveillance Plan. On Wednesday, April 8th, Versar scientists arrived to further assess the situation and discussed plans for the primary phase.

Two days later, State and local officials formed an Intergovernmental Coordinating Group. The purpose of the group was to bring together, in a formal setting, key personnel so there could be direct and effective exchange of ideas and information.

OGS began accepting bids on the Air Pollution Control System (APCS) on July 23rd. The State expected to award the contract within a month's time. The plans for the APCS were developed by Versar, Inc., for the Office of General Services. This system was designed to control the flow of air in the building by drawing it through a series of filters to remove pollutants and toxic substances including dioxins and PCBs in both particulate and vapor phases.

The second Intergovernmental Coordinating Group meeting was held on August 10th in Binghamton. The meeting was presided over by the Executive Deputy Commissioner of OGS, and representatives from the Departments of Health, Environmental Conservation, Labor, the Office of General Services, Broome County and the City of Binghamton were present. Both the public and the press were invited to the meeting. Topics on the meeting agenda included medical surveillance program, the air pollution control system and the biological and chemical tests conducted by DOH.

The week of August 10th, as part of the Health & Safety Plan, OGS awarded the contract for the construction of a trailer (entrance module) which would control all passage into and out of the building. The trailer would be equipped with showers, decontamination areas, appropriate receptacles for the disposal of contaminated protective clothing and laundry facilities.

On Tuesday evening, August 18th, 1981, a public meeting was held in Binghamton to answer citizens' questions regarding any aspect of the State's plans or activities relating to the State Office Building. The meeting was presided over by the Commissioner of the Office of General Services. The Commissioner of Environmental Conservation was also in attendance along with Health Department staff and physicians. The Health & Safety Plan and the Air Pollution Control Plan were presented and discussed. The following week, the Department of Health Commissioner held a meeting with the editorial board of the local newspapers to inform them of the state activities and to clarify any pertinent matters.

Toward the end of the month of August, the Office of General Services completed an Environmental Quality Review Act. The assessment concluded that the primary clean-up phase of the Binghamton State Office Building would not have any significant adverse effect upon the environment.

The construction of an access corridor to connect the trailer to the building, began on the week-end of August 29th. Workers readied the rooftop for the Tuesday installation of the air filtration system. At this same time, a medical surveillance program was initiated for all personnel who would enter the building for proposed activities outlined in the Health and Safety Plan.

On Tuesday, September 8th, a helicopter made four trips to the roof of the State Office Building lifting two 2500 pound filtration units and two pallets of associated equipment.

Later in that month, equipment was moved into the building for tests of the filtration system. In accordance with the Health and Safety Plan, six engineers entered the building to monitor the testing and a Health and Safety Officer was present. By the end of the month, the completed trailer arrived and was connected to the building at the point of the corridor which had previously been constructed.

The RFP for primary clean-up of the building was developed, put to bid and awarded. Allwash, Inc. of Syracuse, N.Y. was the successful low bidder. The primary clean-up consists of three activities: the first, completing the initial clean-up within the building; the second, removing soot from ceiling panels and surfaces above those panels; and third, cleaning elevator shafts and mechanical chases.

By month's end, a DOH physician had begun to hold regular Thursday and Friday office hours in Binghamton for the purpose of counseling and advising any person having health-related questions or any inquiry concerning the Department of Health's medical surveillance program.

In early December, tests performed on areas of the basement parking garage were analyzed. The area was determined to be clean and parking was allowed in those areas.

The on-going testing of the venting efficiency of the Air Filtration Pollution Control System was completed. Results of the extensive testing showed that the system worked effectively.

In discussions with the County consultant, additional monitoring procedures were developed. After review of all data and a general announcement, the venting of the building through the Air Pollution Control System (APCS) commenced February 1, 1982. The primary clean-up phase commenced and is following the procedures outlined in the applicable plans.

Safety of Personnel

The entry module provides for the safe entry and exit of those who must enter the building and is constructed to include entry facilities, locker areas, showers, rest rooms and security offices. The trailer is located at the basement level loading dock. The APCS creates a negative pressure throughout the building and entry module insuring that the flow of air is from the outside of the building, through the building, and finally filtered through the APCS on the roof.

All personnel entering the building must wear protective clothing and a full face respirator. The special clothing comprises socks, underwear, sneakers and rubbers, coveralls, an outer "Tyvek" protective suit and both cotton and rubber gloves. The respirator weighs approximately four pounds and features both activated carbon and high efficiency particulate filters. As personnel exit the building through the module, all protective clothing is removed and thorough showers are taken. Respirators are cleaned and their filters are replaced for future use. The outer suit, gloves and respirator filters are disposed of after each use.

Security

To insure maximum control of movement into, within and out of the structure, 24-hour a day security is maintained. Not only does the security staff regulate personnel movement, but also issues and inventories proper safety clothing and equipment.

All security systems are tested twice weekly and are monitored by personnel in the central security office. The fire and smoke alarm system will be automatically activated in the event of any fire or smoke emergency in the building. Five doors in the building are designated as emergency exits and are wired for an alarm to sound should they be tampered with or opened for any reason.

Pressure gauges monitor the operation of the APCSs. The apparatus is checked daily and, if for any reason the APCS should malfunction, the monitoring devices would automatically notify the security office of the problem and shut the APCS down. In the event of a system malfunction, a magnetic door, located in the entry module, would be released and shut automatically, to prevent any backflow of air from the building to the outside.

Testing for Contamination

Over 265 small bottles and 30 large containers of soot from the building have been collected and delivered to the State Department of Health for use in the testing process. Additional soot samples are being collected on a regular basis from above ceilings and other areas.

The APCSs are constantly cleaning the building's air as it filters through both carbon and high efficiency particulate filters for purification before its release to the atmosphere. Periodic testing of the air moving through the system is performed and the system's filters are checked and replaced as required.

Since considerable volumes of waste water are generated by the cleaning procedures, a water treatment system is in operation at the sub-basement level of the parking garage. This system consists of three above-ground swimming pools, each having a capacity of 13,000 gallons. The water is collected in one tank and runs to the second tank through high rate sand filters which remove large particulates. The water then travels through a series of activated carbon filters that remove dissolved contaminants. The filtered water is discharged into the sanitary sewer system of the city after it is found to be purified in accordance with the terms of the permit issued by the City of Binghamton.

TYPING GUIDE SHEET

Restoration and Operation of Building System

Electrical power was partially restored soon after the fire in February of 1981. Since that time, full electrical power with temporary equipment has been restored and is being maintained.

The heating, ventilating and air conditioning system (HVAC), which is crucial to the clean-up, has been successfully restored to service. At present, the building temperature is being maintained at between 50 and 60 degrees to allow cleaning personnel dressed in several layers of non-porous and therefore hot clothing to efficiently proceed with the clean-up.

The elevator system has been restored in phases over the past few months so that the system is currently providing service that fulfills the requirements of cleaning personnel.

All building systems are operating at levels that are satisfactory to the overall cleaning operation.

Operating Procedures

Maintenance and operations personnel test and ready the building systems each day before the initial entry to the structure. Five cleaning "teams", each consisting of 11 personnel, including one foreman, then begin their work. Since no personnel are allowed to remain inside the building for longer than 4 hours at one time, the cleaning crews work in shifts of approximately 3 hours and 50 minutes each. In addition to the cleaning personnel, there are 5 State inspectors in the building during each shift. They insure that the work already completed and the work in progress is in accordance with the clean-up standards.

As a means of both basic cleaning and preparing the building for more intensive cleaning, all furniture has been vacuumed and removed from all floors and placed in the sub-basement area. The following account of the

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amount of furniture and equipment vacuumed and relocated shows the magnitude of the preliminary work:

930 desks
522 tables
850 file cabinets
110 map files
100 lockers
120 racks
5 microfiche readers

1,950 chairs
325 bookcases
310 storage cabinets
190 stools
52 benches
50 couches
15 computer terminals

200 typewriters
15 postage machines
15 copiers
90 recorders
20 postage scales
40 adding machines
400 miscellaneous items

Many other small items have been compacted and are destined for disposal.

Removal of draperies, carpets and blank ceiling panels has been accomplished to provide for the most meticulous clean-up. These materials, as well as loose paper and desktop items, have been removed to a secure landfill at Niagara Falls. As of October 28, 1982, 1,327 fifty-five gallon drums and approximately 1,200 cubic yards of material had been removed.

Since the building is not perfectly square, the ceiling pieces had been customized for each floor. As pieces are removed and cleaned, each is coded in a way that will allow for its potential reuse.

Many of the cleaning activities are intricate. For example, the cleaning of the light fixtures and air conditioning terminals, by workers dressed in protective clothing, including two pairs of gloves, is an arduous and time consuming task.

A vitally necessary project was and is the positive identification of all areas within the building. Since it is crucial that all personnel speak precisely and in common terms when speaking of the building, all offices and spaces within the building have been identified in a systematic, and certain manner. The scheme for location identification has resulted in the highest degree of control of information regarding clean-up accomplishments.

There are two areas of the clean-up operation that represent major tasks in their own right. The first is the cleaning of intricate heating/cooling

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terminal boxes which includes the opening of the box, removal of insulation, cleaning of the box and its closing. Given the restrictions placed upon clean-up personnel by both the required protective clothing and the various small parts of the terminal boxes, the cleaning of such boxes takes a relatively long time. There are a total of 820 perimeter boxes with another 220 installed in the ceiling.

The second is the cleaning of light fixtures which number approximately 285 on each of the 18 floors. It takes nearly 90 minutes to prepare one fixture for cleaning - that is to take it down, open it and take out the lighting element. It then takes over 2 hours to thoroughly clean the fixture and the tracks in the ceiling that hold the fixture. The time consumed then equals roughly 5,100 fixtures times an average 4 hours per fixture, or 20,400 man hours for this activity alone.

Preparation, cleaning and inspection represent a work day time span from approximately 6 a.m. through 5:15 p.m.

Furthermore, the State´s constant demand for the highest quality work requires - in every respect - a methodical and meticulous process that cannot be rushed.

Records Destruction

Since the contamination within the building had affected the records and other work papers kept in the building, the State Department of Health advised that it would not be feasible to attempt to clean the documents. Accordingly, the decision was made to destroy all paper records.

All documents scheduled for destruction have been shredded or baled and, if they are of a confidential nature, their destruction by shredding has been confirmed by witnesses. At the request of the State Attorney General, a limited number of documents have been located, segregated and temporarily stored in the sub-basement due to their importance with regard to pending litigation. All contaminated materials - in whatever form they take - will be transported to and disposed of at a secure disposal site.

9th and 16th Floors Used as Sample Areas

Both the 9th and 16th floors of the building have been completely cleaned and serve as sample areas, while also providing personnel with the opportunity to experiment with different testing and cleaning techniques. Various experimental cleaning methods have been employed on the sample floors and those that prove successful will be used on the building's other floors.

The following is a listing of several activities and accomplishments, which help illustrate the amount of work being performed inside the building as of the week ending January 31, 1983:

- inventory of all equipment and records in building
- removal of all furniture and office equipment to sub-basement
- opening of duct shafts to allow for cleaning
- shredding and baling of all paper materials
- removal of all carpet
- removal of all bathroom and corridor accessories
- installation of temporary core lighting on floors 3 through 18
- access and removal of exhaust ducts from rest rooms
- preliminary vacuuming of exhaust duct shafts on mens' room side
- removal of secondary duct work in basement
- removal of insulation from terminal boxes in basement
- removal of records and shelving from DOT storage room in basement.

In the concluding stages of the preliminary clean-up operation, activities and actions were initiated to restore the Binghamton State Office Building to a normal operating mode. Activities undertaken can be classified into two major groups:

1. Mechanical/Operational activities
2. Medical/Scientific activities

The following items represent some of the activities which need to be completed to ready the building for reoccupancy from a Mechanical/Operational perspective:

1. The current primary cleaning activity consists of the washing and vacuuming of all office areas of the building to achieve a high level of cleanliness. This activity included the removal of all furniture from the floors as well as the removal of carpeting, draperies, and other appointments. Additionally, lighting fixtures and terminal boxes were removed from their normal stations, completely cleaned and returned to their proper location. The existing vinyl and ceramic tile flooring will also be removed.

2. As the primary cleaning program draws to conclusion, the Binghamton State Office Building is then divided into basic work areas as follows:

   1. Upper Area - floors 2-18
   2. Lower Area - below the second floor

The establishment of these areas enable the workmen to more expeditiously function in the Upper Area while more extensive cleaning activities take place in the lower area.

3. Upon establishing that the air in the Upper Area meets the pre-established standard for cleanliness, the need to continue air filtration in that area will be unnecessary. This will permit the reconfiguration of the APCS to reestablish normal building ventilation in the Upper Area. The APCS units on the roof will be relocated adjacent to the basement area to provide ongoing effective air pollution control for the Lower Area of the building as they have for the entire building in the past.

At the same time, workmen will no longer be required to wear the full range of protective equipment in the Upper Area.

4. Once the Upper Area is established as above described, workmen may begin their activities at a regular pace expediting the rate at which building work may continue.

Service projects to be completed in this phase are related primarily to the restoration of mechanical areas which were opened for cleaning to insure against the exfiltration of any foreign materials which may be left as a result of previous activities.

It is anticipated that all of these restoration activities will take approximately 18 months to 24 months to complete from the date on which they are begun.

5. While the Upper Area projects are being completed as described above, the Lower Area will receive a thorough cleaning in accordance with the provisions of the Health and Safety Plan which had previously been in existence for the entire facility. Workmen will continue to wear protective clothing and utilize the entry module to insure maximum safety and the APCS will function as in the past. While the workmen are active in this phase, they will be cleaning walls, ceilings and all other surfaces in the Lower Area.

Upon completion of this cleaning phase, a new electrical transformer and related building mechanical and electrical equipment will be installed.

Waste material shall be concurrently removed to appropriate landfills.

It is anticipated that this Lower Area activity will take about 18 to 24 months for completion.

While the ongoing work continues at the Binghamton State Office Building, there will be significant additional activity, on an integrated basis, in the Medical/Scientific areas related to the ultimate restoration of the facility to use as follows:

1. Air sampling which was completed late in 1982 for dioxin and dibenzofuran will be repeated with the air handling systems of the building in operation. Air sampling will be conducted in the normal operating zones of the heating, venting and air conditioning systems to insure that comprehensive results are available for review. All results will be transmitted to the Expert Panel for their comments and critique.

The first round of samples indicated that the furan levels were bracketing the levels established for reentry and that dioxin was not detectable at the limits which were the capacity of the testing machinery. Repetition of the samples with the air handling systems in operation and the taking of greater air volumes will allow for analysis and determinations which are representative of the air in the facility as a whole. Results of these tests will guide the State in the final rehabilitation of the facility.

2. Similarly, the ongoing tests conducted on the operation of the APCS will continue for the entire period during which the APCS is utilized.

3. The development of a new wipe sample test is being continued, to most closely duplicate the actual condition of everyday work life. Similarly, the continuous monitoring of waste water and the sampling of water utilized in the cleaning and held for purification and disposal will continue throughout the utilization of the waste water treatment system.

4. The Medical Surveillance Program for workers will continue to operate in accordance with the Health and Safety Plan, thereby requiring bimonthly physicals for those entering the lower area of the building and subsequent final and follow-up physical examinations upon completion of a worker's assignment within the Binghamton State Office Building.

5. Further, the monthly industrial hygiene samples which now show the PCBs levels below all previously established standards (at 0.2-0.3 mcg/m^3) will be continued as work in the building moves forward.

Financial Data

The restoration of the Binghamton State Office Building is expected to cost approximately $24 million. This sum reflects payments for the Health and Safety Program, building security, field operations, engineering consultations, investigations and risk analyses, waste removal planning, APCS, design fabrication, water treatment and sampling and analyses; testing, the purchase and installation of the building entry module and support facilities; installation of special security and alarm systems; boiler repairs, chiller repairs and elevator equipment cooling; emergency electrical work, renovations and repairs at the Christopher Columbus School to provide alternate office space; the primary clean-up contract, equipment, materials, and staff; waste disposal, etc.

Clean-up at the San Francisco One Market Plaza Office Building PCBs Transformer Fire Site

Clean-up of the site commenced on May 16, 1983. Pacific Gas & Electric's (PG&E) clean-up contractor for the project is I.T. Corporation. The building owners retained B.M.S. Catastrophe, Inc., to conduct a clean-up of Floors 2 through 6 and stored tenant materials, to photocopy stored documents, and to direct restoration of the air handling system.

The building was evacuated and sealed off during the fire. Areas exhibiting surface contamination outside the building, were also cordoned off pending clean-up. After extensive air and surface testing indicated no contamination, most ground-floor areas and all of Floors 7 through 28 were opened to normal occupancy on May 25, 1983. Portions of Floor B-1 were also opened at that time. Floors 2 through 6 remain closed pending restoration of the air handling system. Floor B-2 and portions of Floor B-1 remain closed pending the results of the sampling after clean-up.

The methods of clean-up or decontamination employed depended on the surface involved and the level of contamination. Vacuuming was the first method used on surfaces such as concrete floors and walls, metal ducts, switch gear, and sheetrock walls. Further cleaning included wiping these surfaces with L.O.C. (Amway), Penetone Power Cleaner 155, or freon when vacuuming was not sufficient.

The clean-up of the 250,000 square feet of Floors 2 through 6 by B.M.S. Catastrophe, Inc., took seven months and cost $10 million. Complicated items to clean, such as cooling coils, electrical switch gear and electronic control panels were cleaned using a high pressure freon spray. Concrete floors were further cleaned when necessary, by coating with a peelable adsorbant which was peeled off to remove any remaining contamination. Concrete surfaces in proximity to the vault were painted with a sealant as a post-cleaning measure. The vault itself was virtually rebuilt due to the high contamination levels. Reinforced concrete surfaces in the vault were sandblasted, jackhammered and scabbled to remove contamination. Concrete block walls were torn down and replaced.

Three charcoal air cleaning systems were used to remove airborne contamination, and to filter air released to the atmosphere. Removal efficiencies of these systems were generally greater than 99.9 percent for air released to the outside.

For final disposal of hazardous waste solid and low-level wastes, the waste was transported by registered hazardous waste hauler to the Kettleman

Hills Disposal Facility near Kettleman City, California operated by Chem-Waste Management or to the Casmalia Disposal site near Santa Barbara, California. High-level liquid wastes were shipped for incineration at EPA-approved sites.

A BRIEF REVIEW OF DISPOSAL TECHNOLOGY FOR PCBs-CONTAMINATED MATERIAL

As regulations governing the disposal of PCBs and PCBs-contaminated equipment grow more stringent, a number of technologies and methods have been developed to destroy and dispose of PCBs. They include:

(1) Chemical Waste Landfills
(2) Chemical Methods
(3) Land-Based Incineration
(4) High Efficiency Boilers and Cement Kilns
(5) At-Sea Incineration.

Chemical Waste Landfills

From a practical point of view, the most effective method currently available by which a PCDDs- and PCDFs-contaminated waste could be secured is disposal in approved hazardous waste landfills. For instance, solid and low-level contaminated wastes from the One Market Plaza San Francisco clean-up operation were disposed in the Kettleman Hills Disposal Facility near Kettleman City. The integrity of the landfill is influenced by the type of material used to line the landfill. Clayey, silty, and alluvial soils have a strong affinity for TCDD. This affinity has been demonstrated in areas where TCDD contamination has become well known, such as Seveso, Italy (ICMESA), and Aurora, Missouri (Denney Farm Site). The appropriate liner material would thus function as an adsorbent as well as a flow barrier for contaminants which escape from their original containers. Waste containing oils and solvents which might increase the mobility of PCBs, PCDDs, and PCDFs in soil should not be disposed of in the section of the landfill containing contaminated material from transformer/capacitor fires.

Chemical Methods

Alkaline dehydrochlorination is a generic term for several new chemical processes for treating hazardous chlorinated hydrocarbon liquid wastes, including PCBs. Of the many processes, only the Vertac Chemical Company of Memphis, Tennessee, process has been tested on TCDD and other chlorinated dioxins. The other processes are designed to treat PCBs.

The Vertac process involves the dehalogenation of chlorinated dioxins with anhydrous alkali metal salts of polyhydroxy alcohols at atmospheric pressure. Dehalogenation may also be accomplished by reacting a mixture of chlorinated dioxins, an alcohol, and a water solution of an alkali metal hydroxide. Vertac claims that 2,3,7,8-TCDD and chlorinated dioxins concentrations are reduced to essentially zero (2).

The Goodyear Tire and Rubber Company has invented a process to remove PCBs from heat transfer fluids and claims that it reduces PCB levels to less than 10 ppm from a high level of more than 500 ppm (3). It appears to be based on research conducted earlier by Oku, et al. (4), where sodium naphthalenate was found to be a remarkable dechlorination agent for PCBs.

The Franklin Institute has developed a similar process for alkaline dehydrochlorination of PCBs (5). The process first makes sodium glycolate (NaPEG) from molten sodium and polyethylene glycol. NaPEG acts as a superbase and reacts with chlorine atoms in PCBs. NaPEG-containing PCBs go to a separate vessel and are exposed to air; and oxygen completes the PCBs breakdown. Any remaining chlorine is replaced by oxygenated compounds which form oxygenated biphenyls; sodium chloride is the by-product. In tests with soils, NaPEG has reduced PCB concentrations from 1,000 ppm to 481 ppm after 53 days. One drawback with NaPEG is its inability to function effectively in soils containing more than 7% moisture (6).

Sunohio has also developed a reagent process for treating PCBs and has developed units that can be mounted on tractor trailers and moved to a waste site. Sunohio claims that its process reduced PCBs levels in transformer oil

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from 1,000 ppm to 1 ppm and from a high of 10,000 ppm to 50 ppm--all in one pass (3). The Sunohio PCBX process has received EPA approval as a means of removing PCBs from transformer oils.

Ontario Hydro has developed a process where PCBs destruction is achieved by reaction with molten sodium. In this process water content of askarel-contaminated oil is reduced to less than 100 mg/kg. PCBs and other chlorinated compounds are then destroyed over a period of 15-60 minutes by reacting them with finely dispersed molten metallic sodium at temperatures in the range of 120-140°C. The mixture is then centrifuged to remove excess sodium, insoluble reaction products and sludge.

Westinghouse research has found that PCBs can be dechlorinated by using sodium hydride and alkylamine. This process (if found feasible) has a rapid reaction rate under relatively mild conditions. It is inexpensive with common and available reagents and does not require special pressure vessels (7).

Acurex Waste Technologies, Inc., and SED, Inc., have developed sodium-based reagents to treat PCBs. Acurex is building a portable 250 gal/hr demonstration unit to be mounted on a 35-foot long trailer; SED is building a waste treatment plant in Greensboro, North Carolina (4, 8).

Finally, professors at the University of Georgia have reported that there are over 20 different bacteria capable of breaking down PCBs into water and carbon dioxide in 90-130 days (9). They are presently looking at ways to speed up the process. General Electric has already patented a bacteria that consumes oil (10). Another firm, Polybac Corporation, has several organic spill control products on the market that employ the use of microorganisms to degrade oil. The products contain stabilized microbial organisms in suspended animation. The organisms when hydrated on spills of oil reactivate and metabolize spilled materials (10).

Land-Based Incineration

Highly contaminated wastes can be destroyed in incinerators. The incineration process is quite complex and the destruction efficiency depends on the physical and chemical characteristics of the waste, the combustion temperature, residence time and feed conditions. Since the design features and capabilities of the major types of incinerators differ widely, no single incinerator can be used for all wastes. For each type of waste, the right incinerator must be used under the correct temperature and residence time conditions in order to achieve complete waste destruction.

At least two commercial incinerators have been authorized by the USEPA for PCBs destruction -- one at Deer Park, Texas, and the other at El Dorado, Arkansas. Test burns at the El Dorado site showed that 99.9999% of PCBs and their toxic by-products were destroyed, and dioxins and furans were detected at the very low ppb levels.

High Efficiency Boilers and Cement Kilns

The disposal alternative of using high efficiency boilers is restricted to PCB-contaminated mineral oil of low PCBs concentration (50-500 ppm) and offers a substantial reduction in disposal costs.

According to the USEPA's final ruling on the disposal of PCBs, waste oils that contain PCBs in the range of 50-500 ppm can be fired with fuel oil and burned in a high efficiency industrial boiler (11). In May 1980, waste oil containing approximately 500 ppm PCBs was co-fired in accordance with the applicable state and federal regulations. This combustion took place in a high efficiency boiler owned by General Motors Corporation in Bay City, Michigan (12). PCB destruction efficiency was determined to be $\geq$ 99.99% during the evaluation. Boiler residue PCB level was < 1 ppm. No TCDD or TCDF was detected in stack samples at the limits of detection.

The USEPA is also conducting tests for incineration of wastes using cement kilns. If these tests prove successful, cement kilns may also be employed in the future for the destruction of PCBs-contaminated material. Limited duration trials with PCB wastes have taken place outside the U.S.

Besides the obvious economic reasons for a cement plant to engage in PCB-waste disposal, a number of complications are associated with the procedure. These include:

- confidence in staff industrial hygiene safety
- control of variable quality of the second fuel
- potential for rings and plugging due to excessive chlorine
- need for extensive contingency plans
- control of waste transportation traffic
- management of analysis requirements and inventories
- impact of public controversy on basic business.

At-Sea Incineration

At-sea incineration of combustible chlorinated waste has been carried out for many years in Europe aboard incinerator ships, most notably the K/B VESTA. Incineration-at-sea of chlorinated dioxins-contaminated materials was first performed in 1977, aboard the vessel M/T Vulcanus. This ship was utilized to incinerate three shiploads of Agent Orange, totalling 10,400 metric tons, in the Pacific Ocean west of the Johnston Atolls. More recently, the M/T Vulcanus has been employed for the incineration of PCBs.

The M/T Vulcanus is the only incineration vessel that has been employed to incinerate PCBs and chlorinated dioxins-contaminated materials. Additional ships are expected. At-Sea Incineration, Inc. of New Jersey, supported in part by the U.S. Maritime Administration, has announced plans for the construction of ships specifically designed for chlorinated hazardous waste.

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